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CYANIDATION
of
CUPRIFEROUS GOLD ORES

by
H.J. Chalmers & R.M. Lauer

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The undersigned hereby certify that they have read and recommend to the Committee on Graduate Studies for acceptance, a dissertation on "Cyanidation of Cupriferous Gold Ores" submitted by Herbert James Chalmers, B.Sc. and Randolph Mathias Lauer, B.Sc., in partial fulfilment of the requirements for the degree of Master of Science.

Professor..K A Clark..........

Professor..J A Allan..........

Professor......[illegible]

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CYANIDATION
of
CUPRIFEROUS GOLD ORES

By

Herbert James Chalmers

and

Randolph Mathias Lauer

Department of Mining and Metallurgy

University of Alberta

A THESIS

Submitted to the University of Alberta
in partial fulfilment of the requirements
for the degree of Master of Science.

Edmonton, Alberta,

April 1947

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CYANIDATION OF CUPRIFEROUS GOLD ORES

Table of Contents

Page

PREFACE AND ACKNOWLEDGEMENTS

INTRODUCTION 1

THEORY OF THE CYANIDE PROCESS 4

- I DISSOLUTION
  - A Dissolution Equations and Thermodynamic Considerations
  - B Factors Affecting Dissolution
- II PRECIPITATION
  - A Mechanism
  - B Methods of Precipitation
  - C Factors Affecting Precipitation
- III CYANIDE REGENERATION
  - A Natural
  - B Artificial
- IV SUMMARY

CYANIDATION AND THE COPPER MINERALS 65

- I THE COPPER MINERALS
- II COPPER SOLUBILITY AND SOLUBILITY FACTORS
  - A Mechanism
  - B Solubility Factors
  - C Previous Experimental Work
- III METHODS OF RENDERING COPPER INACTIVE
  - A Removal
  - B Control
  - C Cyanide Regeneration

Page

OUTLINE OF POSSIBLE INVESTIGATIONS 100

I CHEMICAL

- A Oxygen and Cyanide Concentrations
- B pH and Oxidizers
- C Temperature
- D Precipitation
- E Mineral Coating
- F Catalysis

II ELECTROCHEMICAL

III PHYSICAL

- A Degree of Grind
- B Time of Contact

EXPERIMENTAL WORK 109

I LABORATORY PRECEDURE

- A Detailed Description of Cyanidation Charge
- B Details of a Test
- C Methods of Analysis and Recording of Data

II INVESTIGATIONS

DISCUSSION, SUMMARY AND CONCLUSIONS, RECOMMENDATIONS ... 226

I DISCUSSION OF INVESTIGATIONAL RESULTS

II SUMMARY AND CONCLUSIONS

III RECOMMENDATIONS

APPENDICES 242

REFERENCES 248

PREFACE AND ACKNOWLEDGEMENTS

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INTRODUCTION

INTRODUCTION

The purpose of this thesis is twofold; first, to present a review of pertinent literature on cyanidation and second, to report the writers' investigations on the effect of copper in the cyanidation of cupriferous gold ores.

In reviewing the literature on cyanidation it was soon appreciated that the theory of cyanidation, until recently, has been the neglected phase of the cyanide process. While the fundamental mechanism of gold dissolution by cyanide solution has been recognized since the inception of the process in the middle of the last century, it was not until the last decade that the theoretical confirmation was expounded. The theories of all important control features of the process have been the postulations of confused thinking, resulting in many conflicting ideas and beliefs. This condition has been fostered by the intricate nature of the treated ores and by the slightly better than superficial knowledge of chemistry of the investigators. To date, all the text-books have stressed the practical application rather than the theoretical side of the subject. Recent application of principles of physical chemistry, in particular thermodynamics, has helped to clear up many of these anomalies. So it was thought that a review of the literature of cyanidation might best be presented

as a treatise on the theory of cyanidation which consolidates all the recent developments.

The frequency of occurrences of copper minerals in gold ores, the difficulties encountered in the cyanidation of such ores, and the lack of success in solving many of these difficulties prompted investigations into the effects of various factors on gold recovery and cyanide consumption in the cyanidation of cupriferous gold ores. In order that these factors might be better appreciated an extensive study of the chemistry of copper relating to cyanidation was made. In addition, the literature dealing with existing and past practise on non-cupriferous ore was studied to determine its application to cupriferous ores.

Experimental work on cyanidation, in the past, has fallen into two categories; theoretical and practical. The former class embraces experiments, such as the dissolution of pure gold in fresh cyanide solution, aimed to establish fundamental relationships. The latter class is carried out to indicate the most efficient or economical treatment of a particular ore. Many investigators have condemned the first type, because of the complexity of ores they have failed to realize any practical application of the results. The second class has added little to the basic understanding

of cyanidation because too often only positive results have been reported and no great attempt has been made to correlate elementary concepts with the experimental findings.

In this investigation an effort has been made to determine fundamental relationships that might be practically applied to cupriferous gold ores generally. However, interpretation of the results must be considered qualitatively rather than quantitatively, and therefore, the necessity of specific tests on particular ores is not eliminated. It is hoped that the results of this investigation may prove helpful in planning and performing the specific tests.

THEORY
# of the
CYANIDE PROCESS

THEORY OF THE CYANIDE PROCESS

Table of Contents

I Dissolution

- A Dissolution equations and Thermodynamic Considerations
- B Factors Affecting Dissolution
    - (1) Cyanide Strength and Temperature
    - (2) Alkalinity
    - (3) Oxygen and Oxidizers
    - (4) Sulphide Ion
    - (5) Addition Reagents
    - (6) Base Metals
    - (7) Electrochemical Reaction

II Precipitation

- A Mechanism
- B Methods of Precipitation
    - (1) Zinc
    - (2) Aluminum
    - (3) Charcoal
    - (4) Electrolytic
- C Factors Affecting Precipitation

III Cyanide Regeneration

- A Natural
- B Artificial

IV Summary

THE THEORY OF THE CYANIDE PROCESS

The cyanidation of precious metal ores involves numerous chemical reactions, some of a very complex nature. A knowledge of these reactions, their products and influencing factors, are important in working out the most economical conditions for cyanidation.

In general the cyanide process comprises three main operations: dissolution, precipitation, and cyanide regeneration. These will be discussed in turn, with reference to work done by other investigators.

I DISSOLUTION

A. DISSOLUTION EQUATIONS AND THERMODYNAMIC CONSIDERATIONS

The simplest form for the dissolution of gold in dilute cyanide solutions may be expressed as follows:

$$Au + 2CN^- = Au(CN)_2^- + e$$

However, several mechanisms have been proposed for the dissolution of gold. Elsner (37), MacLaurin (38), Christy (39) and Bedlaender (40) have shown that oxidation by oxygen or some other reagent is necessary in the cyanide process. For example, Elsner represents the dissolution of gold by the following equation:

$$4Au + 8KCN + O_2(aq) + 2H_2O = 4KAu(CN)_2 + 4KOH$$

Bodlaender suggests that the dissolution of gold proceeds according to the following equations:

$2Au + 4KCN + O_2 + 2H_2O = 2KAu(CN)_2 + 2KOH + H_2O_2$

The hydrogen peroxide formed, is used in the reaction:

$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH$

The overall equation is the same as that given by Elsner, however, Bodlaender was able to account for as much as 75% of the hydrogen peroxide given by his first equation. This would tend to indicate that Elsner's equation is not strictly correct.

Janin (41) suggests that gold is dissolved with the liberation of hydrogen according to the equation:

$2Au + 4KCN + 2H_2O = 2KAu(CN)_2 + 2KOH + H_2$

Janin's equation does not appear to represent correctly the dissolution of gold, in that, no hydrogen has been detected in the ordinary alkaline cyanide solutions, although it is possible that the hydrogen might unite immediately with oxygen to form water and thereby escape detection.

Barsky et al (1) attacked the problem of determining the most probable equation for representing the dissolution of gold, by an application of the theory of "free energy change" to the different chemical reactions. They state, "It is possible to determine whether or not a given reaction will theoretically take place by calculating the free energy of the reaction. This free

energy value for any given reaction is the algebraic sum of the free energies of formation of each of the reactants and products and if these values are known the calculation is simple. A chemical change always involves an energy change and the amount of energy change involved is the factor determining whether a given reaction will take place or how far it will go. In chemistry we consider what is known as the free energy, that is, the maximum amount of energy that can be utilized as work or be transformed into a form of energy other than heat. This energy can be measured by means such as we have used here."

With this data on free energies the equilibrium constants of the various equations proposed were calculated, the equilibrium constant being a gauge of the completeness of the reaction.

For Elsner's equation:

$$4Au + 8KCN + 2H_2O + O_2 = 4KAu(CN)_2 + 4KOH$$

$$K = 10^{66.0}$$

Similarly for Bodleander's equations:

$$2Au + 4KCN + 2H_2O + O_2 = 2KAu(CN)_2 + H_2O_2 + 2KOH$$

$$K = 10^{16.0}$$ and for

$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH$$

$$K = 10^{49.8}$$

These equilibrium constants indicate that in the presence of oxygen the reactions would proceed practically to completion. Although Elsner's equation gives the same final products as the sum of Bedlaender's equations, it is not strictly correct, because it does not express the intermediate step involving the production of hydrogen

peroxide, the formation of which Bodlaender proved.

For Janin's equation:

$$2Au + 4KCN + 2H_2O = 2KAu(CN)_2 + 2KOH + H_2$$

$$K = 10^{-9.9}$$

Here the equilibrium constant is so very unfavorable that the formation of hydrogen may be considered impossible under ordinary cyanidation conditions.

Thus it would appear that Bodlaender's equations represent the most probable chemical reactions for the dissolution of gold.

B. FACTORS AFFECTING THE DISSOLUTION OF GOLD

1. Cyanide Strength and Temperature

In the early days of cyanidation, cyanide solutions containing 0.25% sodium cyanide and higher were used in the dissolution of gold. With the arrival of fine grinding the strength of solutions was reduced and today most cyanide plants use solutions around 0.05% sodium cyanide.

According to MacLaurin (42) the rate of the solubility of gold in potassium cyanide solutions passes through a maximum in passing from concentrated to dilute solution, with the maximum dissolution occuring at a 0.25% potassium cyanide or an equivalent of 0.19% sodium cyanide solution. Further, MacLaurin explains

that this variation is due to the decreased solubility of oxygen in cyanide solutions with increased concentration.

However, in a more recent investigation on the rates of dissolution of pure gold in solution containing from zero to 0.50% sodium cyanide, with no alkali added, Barsky et al (1) found that the maximum rate of dissolution was obtained with a 0.05% solution of sodium cyanide, which corresponds with concentrations used in modern mill practice. Further, to determine whether there is any relationship between cyanide strength and oxygen dissolved, oxygen determinations were made on the different cyanide strength solutions. Results are tabluated in Table 1. Unlike MacLaurin they found the solubility of oxygen was practically unaffected by the concentration of cyanide.

Table 1 Relative Amounts of Gold Dissolved and Solubility of Oxygen in Cyanide Solutions

NaCN in Solution percent	Gold Dissolved in 1 hr. Mg. per. Sq. cm.	Oxygen per Liter. Mg.
0.500	2.943	8.33
0.250	3.007	8.29
0.100	2.986	7.96
0.050	3.251	8.02
0.025	2.513	7.90
0.010	0.338	8.25
0.0 (distilled H_2O)	---	8.20

Hedley (11) in his investigations similarly noted that the maximum rate of dissolution was obtained for a

0.05% sodium cyanide solution. In addition the solution contained a small percent of sodium hydroxide.

Temperature plays an important part in the dissolution of gold in cyanide solutions. By increasing the temperature the rate of dissolution of gold is increased until a maximum is reached at 85°C. After this point there is a decrease in the rate of dissolution. Also, as the temperature is increased, cyanide consumption is increased. Above 38°C cyanide consumption is quite heavy and would offset any advantage gained by heating cyanide solutions. The most suitable temperatures at which to maintain solutions is between 15°C and 20°C. The increased dissolution of gold and other metals in cyanide solution with increased temperature is illustrated in Table 2 from Mellor (50).

Table 2 The Dissolution of Metals in a 1.86% Potassium Cyanide Solution

Metal	Milligrams dissolved per sq.cm. of surface	
	15.6°	71°
Aluminum	0.096	4.510
Zinc	0.054	0.552
Copper	0.053	1.263
Silver	0.016	0.069
Gold	0.009	0.229
Iron	trace	0.010
Lead	-----	0.031

2. Alkalinity

Although alkalinity does not enter directly into either the dissolution or precipitation reaction, its presence in solution is essential to successful cyanidation. When sodium cyanide dissolves in water, the hydrolysis reaction is,

$$Na^+ + CN^- + H_2O = Na^+ + OH^- + HCN$$

or dropping the sodium ion

$$CN^- + H_2O = OH^- + HCN. \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (1)$$

Now from Prutton and Maron (49)

$$\frac{(H^+)(CN^-)}{HCN} = 7.2x10^{-10}. \;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (2)$$

and for H_2O

$$(H^+)(OH^-) = 10^{-14} \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (3)$$

dividing (2) by (3) we have

$$\frac{CN^-}{(HCN)(OH^-)} = 7.2x10^4 \;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (4)$$

If the OH^- concentration varies then the CN^- concentration must vary. This relation can be further illustrated by the following calculations. Taking a 0.10% cyanide solution (0.0204 Molar) and letting x equal the percent dissociation, we have

$$HCN = H^+ + CN^-$$

$$(0.0204 - x) = x + x$$

For a pH of say 10, the hydroxal concentration

$(OH^-) = 10^{-4}$ from equation (3).

Substituting in equation (4) we have

$$\frac{x}{(0.0204 - x)(10^{-4})} = 7.2 \times 10^{4}$$

Solving $x = 0.0179$

Therefore the percent dissociation for a pH of 10 is $\frac{0.0179}{0.0204} = 87.8$

These calculations were repeated for various pH values and the results drawn up in the accompanying graph -fig. 1.

From the graph it is apparent that a high pH, that is, high OH^- concentration, is preferable in the cyanidation of gold. For example, at a pH of 9 the dissociation of HCN is only 42% of the cyanide strength and although this dissociation is maintained when cyanide is consumed, it is still sufficiently low to seriously retard gold dissolution. Nevertheless, this point may be utilized in controlling the formation of various cyanicides, for example, pyrrhotite. Haden (5) illustrates the importance of alkalinity control in cyaniding a gold ore associated with arsenopyrite and pyrrhotite. The optimum pH value for dissolution was between 8 and 9. For a pH above 10, cyanide consumption increased, dissolution of gold decreased, and the formation of thiocyanates increased. This tends to confirm the hypothesis of the attack of excess alkali on pyrrhotite. Below a pH of 7, cyanide destruction was great due to the formation of

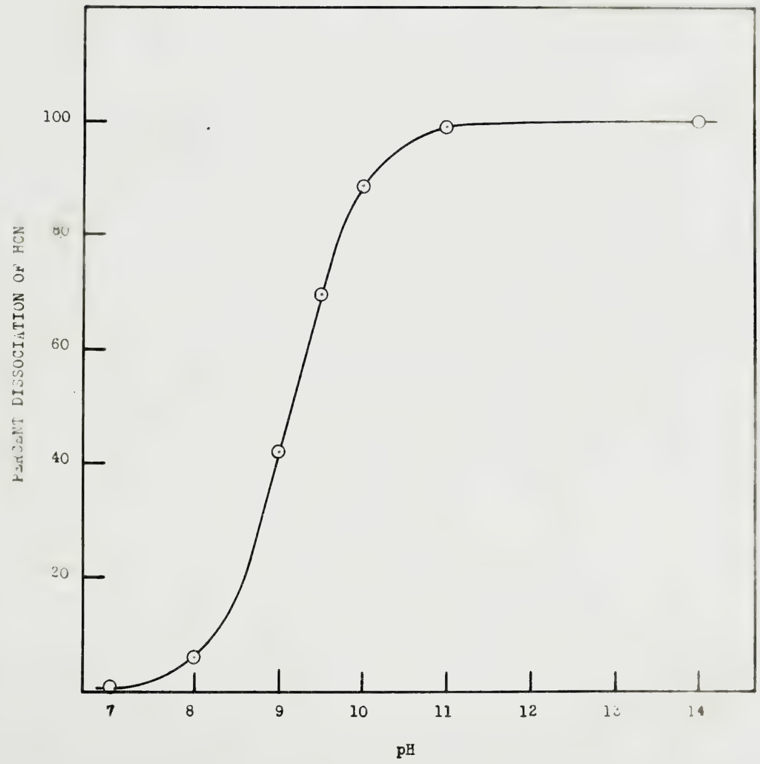

FIG. 1 - RELATIONSHIP BETWEEN pH AND DISSOCIATION OF HCN

ferrocyanides and liberation of HCN.

In the ordinary cyanide process the hydroxyl ion has three principal functions (27):

1. Flocculation of particles of colloidal size, thus increasing their settling rate,
2. Neutralization of the acid forming cyanicides in the ore,
3. Suppression of the hydrolysis of the cyanide salt.

The cyanide salt ionizes in water in accordance with equation (1). The addition of OH^- ions forces the reaction to the left, preventing the formation of poisonous HCN.

As previously indicated in fig. 1, it is apparent that a high OH^- concentration is preferrable for supplying the necessary CN^- concentration (by the dissociation of HCN) for gold dissolution. However, the method of introducing the hydroxyl ion, that is, by CaO, NaOH, Na_2CO_3, etc., is an important factor in the cyanide process. Barsky (1) in his investigation of the effects of alkalinity on the rate of dissolution of pure gold, found that lime, even in small amounts caused a very pronounced reduction in the dissolution of gold, whereas, sodium hydroxide had little effect, requiring very high pH values (above 13) before a serious reduction in the dissolution of gold was affected.

The great difference in the two alkali shows that some other influence besides OH^- ion is at work. By further experimentation Barsky found that the great reduction in the rate of dissolution of gold in cyanide solution by the addition of lime is due neither to lower solubility of oxygen in the solution nor to the presence of calcium ions. Apparently both calcium and hydroxyl ions must be present to produce the full effect.

Fahrenwald (3) similarly found that lime decreased the rate of dissolution of gold very markedly in strong cyanide solutions (6.054 lbs. per ton solution) in cyaniding a silicious gold ore, whereas, NaOH, Na_2CO_3 and $Na_2HPO_4 \cdot 12H_2O$ had little effect on gold extraction. Two facts were brought out by the results of his tests, namely:

1. Alkalinity (pH) cannot be the principal factor causing the decrease in the dissolution of gold or there would be a marked difference for NaOH, Na_2CO_3 and $Na_2HPO_4 \cdot 12H_2O$ since there is considerable difference in the pH of these solutions. (Table 3)
2. Cyanide consumption and rate of dissolution are not directly connected, because both Na_2S and CaO strongly inhibit the dissolution of gold but the cyanide loss in the case of Na_2S is much greater than in the case of CaO. Likewise, there is a great difference in the

cyanide losses in solutions of NaOH and Na_2CO_3, but these two reagents have the same effect on the rate of dissolution of gold (Table 4).

In an investigation on the cyanidation of a pyrrhotite gold ore Gritsuk (14) similarly found that solutions of high lime alkalinity were poor solvents for gold, whereas, if the hydroxyl ion was furnish by sodium hydroxide and the calcium ion by calcium chloride the solution was a good gold solvent. However, a certain minimum lime alkalinity must be maintained. Within the limits studied he found that sodium hydroxide had no effect on gold dissolution and that sodium carbonate counteracted the effect of high lime alkalinity when just sufficient sodium carbonate was added to precipitate the calcium.

A recent innovation in Canadian milling practice was the discovery that good recoveries could be obtained when "air-slaked" lime was used, but the use of water slaked lime led to poor recoveries (6). Air-slaked lime is prepared by, first water slaking in the ordinary way, then spreading it out in the open air in a layer about four inches deep and turning the material over twice weekly for a month.

It has been suggested that the difference in behaviour of the two forms is probably due to the

Table 3. - pH of Solutions in Tests by Fahrenwold

Reagents	Concentration in lbs. per ton of Solution 1	2	3	6	9	12	15	18
$Na_2HPO_4 \cdot 12H_2O$	-	-	10.4	10.4	10.4	10.4	10.4	9.9
Na_2CO_3	-	-	9.8	9.8	9.8	9.6	9.6	9.6
CaO	12.0	12.2	12.4	12.6	12.6	12.6	12.6	12.6
Na_2S	-	-	12.0	-	-	-	12.8	-
NaOH	-	-	12.0	12.6	12.7	12.7	12.7	13.1

Table 4. - NaCN consumption in Tests by Fahrenwold

Reagents	Pounds per ton of Solution Concentration in lbs. per ton of solution 1	2	3	6	9	12	15	18
$Na_2HPO_4 \cdot 12H_2O$	-	-	1.184	1.104	1.154	1.104	1.104	1.184
Na_2CO_3	-	-	1.134	1.654	1.754	2.034	2.494	1.414
CaO	0.674	0.634	0.354	0.534	0.354	0.354	0.254	0.234
Na_2S	-	-	2.794	-	0.234	-	-	-
NaOH	-	-	0.234	0.134	0.134	0.094	0.554	0.474

difference in the $Ca(OH)_2$ and the $CaCO_3$ content. Water slaked-lime would be high in $Ca(OH)_2$ and low in $CaCO_3$. It would supply a powerful soluble caustic alkali, which reacts, in the case cited, with antimony compounds to give solutions detrimental to gold extraction. Air-slaked lime would be low in $Ca(OH)_2$ and high in $CaCO_3$. The $CaCO_3$ is almost insoluble in cyanide solutions but remains in reserve, reacting only to neutralize the ore acidity and not supplying caustic alkali to the solution, to make it a solvent of the sulphides present.

However, an investigation carried out at the Ore Dressing Laboratories in Ottawa by B.P.Cogne does not substantiate this explanation. It was found that when calcite was used, stibnite went into solution to a much greater extent than might be expected from theoretical considerations. Cases are also on record in which the use of lime was found necessary to provide a suitable alkalinity, though the gangue itself was high in limestone.

3. Oxygen and Oxidizers

According to Elsner's andBodlaender's equations oxygen is indispensible in the dissolution of gold. It has been shown that the rate of dissolution of gold, in a cyanide solution of constant oxygen content, increases with the cyanide concentration reaching a maximum and

then decreases for higher concentrations. H.A.White (48) suggests that, since both cyanide and oxygen molecules must appear at the gold surface in the ratio called for by Elsner's equation, the rate of dissolution should be governed by the rates of diffusion of these two species of molecules. Thus, if the cyanide strength and oxygen conentration (pressure) were increased simultaneously in a constant ratio, the rate of dissolution of the gold should be directly proportionate to the oxygen pressure (also to the cyanide strength).

The experimental results obtained by Fahrenwald (3) bear out the above points. He found that the rate of dissolution of pure gold is directly proportional to the oxygen pressure, provided the cyanide strength of the solution is increased in the same ratio as the oxygen pressure. This observation applies to solution containing only cyanide and oxygen. The addition of other substances might cause the curve to deviate from a straight line. Further he found that the rate of dissolution of gold from an ore does not increase in proportion to the oxygen pressure in solution of constant cyanide strength, rather it tends to increase rapidly at first, reach a maximum and then diminish again.

Barsky et al (2) similarly carried out an investigation on the effects of varying amounts of oxygen in

solution on the rate of dissolution of pure gold. They found that the rate of dissolution of gold in cyanide solution is directly proportional to the amount of dissolved oxygen in solution (Table 5). In the tests the gas delivered to the dissolution apparatus was varied from zero, in which nitrogen alone was used, to 99.5% oxygen. It will be noted that gold will not dissolve in dilute cyanide solutions in the absence of oxygen.

Table 5 Rate of Dissolution of Pure Gold With Varying Amounts of Oxygen in Solution

Percent Oxygen	Rate of Dissolution Mgs./Sq.Cm.per hour
0	0.040
9.6	1.032
20.9	2.364
60.1	7.618
99.5	12.62

Barsky's results appear contrary to those of Fahrenwald in that Barsky obtained a direct relation between the rate of dissolution and the partial pressure of oxygen, that is, the amount of oxygen in solution, for a solution of constant cyanide strength, whereas, Fahrewald found that the rate of dissolution of pure gold from an ore does not increase in proportion to the oxygen pressure in solutions of constant cyanide strength, rather it tends to increase rapidly at first,

reach a maximum and then diminish again. However, he did find that the rate of dissolution is directly proportional to the oxygen pressure, provided the cyanide strength of the solution is increased in the same ratio as the oxygen pressure.

This apparent contradiction of investigational results is possibly due to the fact that Barsky investigated dissolution rates with the partial pressures of oxygen below and up to atmospheric pressure, whereas, Fahrewald investigated pressures much higher. Had Barsky's investigations been continued, similar results might have been obtained.

From the preceding investigational work on the dissolution of gold in oxygen-bearing cyanide solutions, the following points are noted:

1. The rate of dissolution of gold, in a cyanide solution of constant oxygen content, increases with the cyanide concentration reaching a maximum and then decreases for higher concentrations.
2. The rate of dissolution of gold in a solution of constant cyanide strength does not increase in proportion to the oxygen pressure, rather it tends to increase rapidly at first, reach a maximum and then diminish again.
3. The rate of dissolution of gold is directly proportional to the oxygen pressure provided the cyanide

strength of the solution is increased in the same ratio as the oxygen pressure.

White (48) has suggested, that since both cyanide and oxygen molecules must be present at the surface of the gold to effect its dissolution, it would appear that the rate of dissolution should be governed by the rates of diffusion of these two molecules. The rate at which the molecules of any particular species arrive at the surface depends on both the species in question and its concentration in solution. If conditions were such that the molecules of cyanide and oxygen appeared at the gold surface in exactly the right proportions the dissolution rate would have a certain figure and this rate would fall off for a decreased rate of supply of either cyanide or oxygen molecules.

White's hypothesis explains the experimental evidence in part only. It accounts for the increase in the rate of gold dissolution with cyanide concentration, reaching a maximum, in a cyanide solution of constant oxygen content. But it does not explain the decrease in gold dissolution, when the cyanide concentration is increased beyond that required for maximum dissolution.

The writers propose the following, that the dissolution of gold in an oxygen-bearing cyanide solution is a heterogeneous reaction of the type including the

solid, ionic and gaseous state. An increase in cyanide concentration beyond that required for maximum dissolution may result in a decrease in the diffusion rate of the oxygen molecules to the gold surface. In other words, a large increase in concentration, with a subsequent increase in the diffusion rate, of one of the molecules is at the expense of the other, resulting in a decreased rate of gold dissolution.

Since oxygen is indespensible in the dissolution of gold by cyanide solution the use of chemical oxidizing agents has found a varied application in increasing the dissolution of gold and the treating of ores presenting special difficulties. Mellor (51) in discussing the investigational results of early investigators notes that ozone, oxygen and hydrogen peroxide accelerate the dissolution of gold. Among the accelerating agents he includes potassium perchlorate, periodate, permanganate, sulfate, ferricyanide and carbonate; sodium sulphate and peroxide, ammonium sulphate; chlorine, iodine and bromine--the most marked action occurring with potassium ferricyanide, potassium or sodium sulphate and sodium peroxide. Scarcely any acceleration was observed with potassium chlorate, bromate or iodate or sodium stannate; while no appreciable change occurs with sodium, cobalt, cupric chloride or with mercuric cyanide. Ammonium

persulphate accelerates the action, while potassium nitrite and ammonium vanadate are indifferent. Organic substances with oxidizing properties raise the solvent action of alkali cyanide on gold, for example, nitroso--B--naphthol nitrobenzene, O--nitrophenol, and picric acid.

Prentice (4) presented a practical method of increasing the oxygen content of cyanide solutions, which is being put into practice on the Rand. There, due to the high altitude, the normal oxygen content of the water is low. By submitting the solution to a pressure of 65 pounds per square inch the oxygen content is increased, with a resulting lowering of tail assays and the remarkable reduction in cyanide consumption of 30%.

Further application of chemical oxidizers is illustrated in an investigation of Leaver (7), in which he found that the harmful effects of soluble lead compounds, due in part to the consumption of oxygen in solution, could be rectified by the addition of artificial oxidizers as sodium peroxide and hydrogen peroxide. Beck (9) similarly found that hydrogen peroxide eliminated the effect of lead salts and alkali on gold dissolution, although oxygen tests prior to the addition of hydrogen peroxide, showed that the solutions were almost completely saturated with oxygen.

To date, the practical application of artificial oxidizers in cyanidation has been limited principally to the use of sodium peroxide and hydrogen peroxide, the failure of similar reagents being chiefly due to their cost or tendency to oxidize cyanides to cyanates which do not dissolve gold.

4. Sulphide Ions

"Sulphide ion retards the dissolution of gold when present in concentration to the extent of more than 5 mg. per liter" (25). Putnam (30) has shown that neither the oxygen depletion nor the thiocyanate formation hypothesis can adequately account for this retardation and suggests that the effect is caused by the adsorption of sulphide ion by the gold at the metal-solution interface, thereby isolating the gold from the solution.

In the literature on cyanidation considerable contradiction is found as to the actual existance of the sulphide ion in ordinary cyanide solutions. Betell (28) states: "it rarely happens that sulphides are present in cyanide solutions." Clennell (29) states, "Soluble sulphides can seldom be detected and in any case, would rapidly be destroyed by conversion into thiocyanates or precipitated as ZnS."

Despite the fact that many investigators have shown that soluble sulphides do not exist in mill solutions,

especially when zinc precipitation is used, there are those who adhere to the idea that the principal function of lead salts in cyanidation is to remove soluble sulphides from the solution. While it is true that lead salts will remove soluble sulphides it seems futile to add lead salts for something which does not exist, except in exceptional cases.

The absence of soluble sulphides in mill solutions is readily understandable from three considerations noted by Clevenger (10) which prevent their accumulation in the solution and actual formation, except perhaps momentarily.

1. Zinc taken into solution during precipitation appears to be as effective for their removal as lead salts added intentionally;
2. Sulphides rapidly form sulphocyanates with the simple alkaline cyanides which are always present;
3. Alkaline sulphides rapidly oxidize to thiosulphates, which in turn probably oxidize to sulphates which cannot rise above a small percentage on account of the slight solubility of calcium sulphate. The instability of soluble sulphides is further illustrated by Clevenger in a case in which Na_2S was deliberately added for another purpose and that by merely decanting from one tank to another, it disappeared.

Thus, it would appear that the retardation of the dissolution of gold by the sulphide ion is definitely

restricted to exceptional cases, as for example, new plants starting up with fresh solution. In any event, its presence can be successfully counteracted by the addition of the proper amount of lead salt.

"The best method available at present for the detection of minute concentrations of the sulphide ion in alkaline cyanide solutions is the nitroprusside test, with a sensitivity of only one part in fifty thousand (26)." Since sulphide ion, when present in concentrations more than 5 mg. per liter (1 part in two hundred thousant), retards the dissolution of gold, this method would seem inadequate to assure the absence of the sulphide ion.

5. Addition Reagents

As early as 1893, MacArthur and Ellis were granted patents for the use of lead plumbate, carbonate, acetate and sulphate; mercuric chloride; manganese sulphate or chloride; ferric hydroxide or oxide, as well as various zincates and other oxides in connection with cyanide solutions for increasing the extraction of precious metals. Cyanogen bromide similarly proved effective in increasing gold extraction in experiments made in 1894 (45). On the whole the mechanism by which these reagents function is not completely understood.

When cyanogen bromide is added to a solution of potassium cyanide the following reactions ensue (45):

$$BrCN + KCN = KBr + 2CN$$

In the presence of metallic gold and an excess of potassium cyanide the further reaction proceeds:

$$2KCN + 2Au + 2CN = 2KAu(CN)_2$$

Or as the two reactions are in reality simultaneous this may be expressed as follows:

$$2KCN + 2Au + BrCN = 2KAu(CN)_2 + KBr$$

A similar but simpler process was used by adding a small amount of dilute bromine water to a dilute solution of potassium cyanide in the presence of metallic gold. The reactions that take place may be analysed as follows:

$$2KCN + Br = KBr + CN + KCN$$

$$Au + CN + KCN = KAu(CN)_2$$

Or as the reactions under favorable circumstances may be simultaneous:

$$2KCN + Au + Br = KAu(CN)_2 + KBr$$

The principle application of cyanogen bromide to date has been in the dissolution of gold tellurides, which are dissolved with the greatest difficulty in ordinary cyanide solutions.

As previously stated the mechanism by which many of these addition reagents function is not completely understood. To this class belong the lead salts, with the largest varied application of all. At first the

practice of adding lead salts to cyanide solutions was commonly understood to be for two main purposes:

1. To precipitate harmful impurities such as soluble sulphides.
2. To increase the activity of zinc as a precipitant.

As to the latter point, it is a common well established fact, although the actual mechanism by which it functions is not definitely established. However, as to the first point considerable contradiction exists, primarily, in that the existance of soluble sulfides in ordinary cyanide solutions is very doubtful. However, the fact that lead salts have been both beneficial and harmful in cyanidation is shown by the results of numerous investigations carried out in this direction.

Clevenger (10) found that lead salts may accelerate the dissolution of silver from ores in which silver occurs as a sulphide through the more prompt removal of the sulfur ion from the system. Gold and silver extraction improved up to 0.5 lb. of lead acetate per ton, while 1.0 lb. per ton almost nullified the effect of the lead salts. Also in certain cases with sulphide ores, lead may effect a saving of cyanide through retarding the formation of sulphocyanate or preventing the separation of elemental sulphur from the solution. (Elemental sulphur, with solutions of the alkaline cyanides, forms sulphocyanates).

Holt (36) has also shown, that the presence of the proper proportion of lead salts greatly accelerates the dissolution of silver sulphide in cyanide solutions, but that lead retards the dissolution of the antimonial compounds of silver.

Johnson (32) states: "The use of lead salts notably renders insoluble, harmful impurities as soluble sulphides and the excess passing through with the solution to the extraction boxes, tends to maintain the efficiency of the couple."

Gritsuk (14), in cyaniding a pyrrhotitic gold ore, found that the use of litharge accelerated the dissolution of gold and reduced reagent consumption considerably. Further, with increasing amounts of litharge the quantities of thiosulphate, thiocyanate and ferrocyanide decreased.

O'Connell (15), in cyaniding a sulphide ore, found that the addition of 0.5 lbs. of lead acetate per ton of ore with excessive aeration a good recovery was obtainable.

Haden (5) investigated lead salts with regard to their buffering action. He found the soluble salts the most active. Litharge had poor buffering qualities but had the advantage of being cheap. In cyaniding an arsenopyrite and pyrrhotite gold ore in the presence of lead, a cyanide solution of pH of 9.6 gave good gold

extraction and low cyanide consumption. As the quantity of lead was increased, so did the relative proportion of the thiocyanate increase over the ferrocyanide in the final solution, while total cyanide consumption was reduced. Still further addition of lead eventually increased the cyanide consumption.

Caldecott (33) states lead salts precipitate soluble sulphides, but the PbS formed is still an absorbent of O_2 and KCN, forming PbO and KCNS.

Leaver et al (7) found that the presence of soluble lead compounds during cyanidation slowed up the rate of dissolution of gold in the usual cyanide solution. They contribute it to the removal of oxygen from the solution and the coating of the gold with insoluble lead compounds. Further they illustrated that chemical oxidizers corrected the harmful effect of lead or by the use of such alkali as sodium hydroxide and sodium carbonate and a pH not exceeding 11, the lead compounds could be rendered harmless.

Beck (9) similarly found that alkali soluble lead compounds were harmful in cyanidation and that hydrogen peroxide eliminated the effect of lead salts, although oxygen tests, prior to the addition of hydrogen peroxide, showed that the solutions were almost completely saturated with oxygen. Beck puts forth a hypothesis to

explain the action of lead salts as follows: the first stage in the dissolution of gold by cyanide is the formation of sodium aurate by oxidation in the presence of hydroxyl ions. This dissolves with the formation of sodium aurocyanide and hydrogen peroxide as in Bodlaender's equation. In the presence of lead salts the aurate is "fixed" as an insoluble lead aurate, which coats the gold and prevents further action by the cyanide.

Von Bernewitz (31) mentions various ores from different parts of the world, in some of which the addition of lead was found useful and in others yielded no apparent result.

Thus it is apparent that the use of lead salts is varied and can only be determined by careful experimentation. To quote Clevenger (10), "It may be said that the advantageous use of lead salts is one of the finer points of the game, and, even in cases where its use might be advantageous, unskilled application may spoil the whole effect."

6. Base Metals

The metals of greatest significance in the cyanide process next to gold and silver are copper, iron, zinc, lead and mercury. They involve chemical reactions in which their complex cyanide and complex hydroxyl ions are formed, causing considerable cyanide consumption.

Of the metals under discussion gold, silver, iron, copper and mercury fom only complex cyanide ions; lead forms only the complex hydroxyl ion; and zinc forms both.

Two general types of mechanism have been postulated for dissolution of metals in an aqueous solution of CN ions: (26)

1. Dissolution in an Oxygen-bearing Solution--Elsner type equation.

$4Cu + 12CN^- + O_2 + 2H_2O = 4Cu(CN)_3^{2-} + 4OH^-$

$2Fe + 12CN^- + O_2 + 2H_2O = 2Fe(CN)_6^{4-} + 4OH^-$

$2Zn + 8CN^- + O_2 + 2H_2O = 2Zn(CN)_4^{2-} + 4OH^-$

$2Hg + 8CN^- + O_2 + 2H_2O = 2Hg(CN)_4^{2-} + 4OH^-$

2. Dissolution in an Oxygen-free Solution--Janin type equation.

$2Cu + 6CN^- + 2H_2O = 2Cu(CN)_3^{2-} + 2OH^- + H_2$

$Fe + 6CN^- + 2H_2O = Fe(CN)_6^{4-} + 2OH^- + H_2$

$Zn + 4CN^- + 2H_2O = Zn(CN)_4^{2-} + 2OH^- + H_2$

$Hg + 4CN^- + 2H_2O = Hg(CN)_4^{2-} + 2OH^- + H_2$

Reynolds (26) calculated the free energy change and the equilibrium constants for the Elsner type and the Janin type equations for copper, iron, zinc and mercury. Along with the Barsky et al (1) values for gold and silver these are listed in the following table.

Table 1 Free Energy Changes and Equilibrium Constants For Dissolution of Metals in an Aqueous Solution of CN- ion

Metal	O_2-bearing Sol'n. Elsner Equation	O_2-free Solutions Janin Equation
Iron	$dF^\circ = -181{,}824; K = 10^{133.0}$	$dF^\circ = -32{,}400; K = 10^{23.7}$
Zinc	$dF^\circ = -156{,}904; K = 10^{115.0}$	$dF^\circ = -19{,}940; K = 10^{14.2}$
Copper	$dF^\circ = -141{,}204; K = 10^{103.5}$	$dF^\circ = -12{,}090; K = 10^{8.9}$
Gold	$dF^\circ = -90{,}036; K = 10^{66.0}$	$dF^\circ = \not- 13{,}494; K = 10^{-9.9}$
Silver	$dF^\circ = -79{,}312; K = 10^{58.1}$	$dF^\circ = \not- 18{,}856; K = 10^{-13.8}$
Mercury	$dF^\circ = -77{,}524; K = 10^{56.7}$	$dF^\circ = \not- 19{,}750; K = 10^{-14.5}$

On the basis of the above thermodynamic data, we may say that: gold, silver and mercury are soluble in an oxygen-bearing solution of CN ions, but are insoluble in an oxygen-free solution of CN^- ions. Zinc, copper and iron are soluble in either an oxygen-bearing or an oxygen-free solution of CN^- ions, but the reaction is more complete in the oxygen-bearing solution.

The theory of free energy change is concerned solely with the change in state between the beginning and the end of the reaction. It gives us no information whatsoever on the speed of the reaction. It would be incorrect to assume, on the basis of the numerical value of the equilibrium constant that one metal will dissolve at a faster or a slower rate than another metal. No

theory of chemical kinetics has yet been developed which would enable one to predict the speed of the dissolution reaction.

The application of the above theoretical discussion on the dissolution of base metals is limited in practice, in that, ordinarily the metals do not occur in their native state, but in the form of various compounds. However, it does give an indication of some of the difficulties that may be encountered in the cyanide process because of their presence.

Investigations carried out on a variety of minerals has revealed important information applicable to ores presenting special difficulties in cyanidation. Leaver and Woolf (12) in an investigation on the solubility of copper minerals, including metallic copper and under the ordinary conditions for cyanidation, found, that azurite, bornite, chalcocite, cuprite, malachite and finely divided metallic copper are readily and completely soluble. Enargite and tetrahedrite are sufficiently soluble to cause an excessive loss of cyanide. Precious metal ores containing small percentages of chalcopyrite or chrysocolla may give satisfactory returns with the usual cyanidation. The ratio of cyanide used to copper dissolved varies for each of the minderals given. It corresponds approx-

imately to an average molecular ratio of 3 cyanide to 1 of copper.

Further tests to determine the effect of copper in cyanide solutions on gold dissolution indicate that the presence of copper up to four pounds per ton of solution has no detrimental effect on gold extraction, provided the solution contains free cyanide equal to the quantity needed in fresh solution to obtain maximum recovery. Sodium-copper cyanide is a weak solvent for gold. Excess lime does not increase the extraction of gold by a copper cyanide solution but an excess of caustic soda greatly increases gold extraction.

Further investigations by Leaver and Woolf (12) on all the common zinc minerals, showed that smithsonite, hydrozincite, and zincite are sufficiently soluble under the usual conditions for cyanidation to cause an accumulation of zinc in solution and thus impair the efficacy of the solution as a solvent for gold. Commercial zinc dust is also readily soluble and therefore an excess over that necessary to precipitate the gold should be avoided. The double sodium zinc cyanide by itself is a weak solvent for gold and silver but the addition of lime or caustic soda liberates some free cyanide that will increase the efficacy of the solution. However, the zinc must be removed to obtain maximum dissolution

of precious metals.

Cyanidation tests conducted by Hedley (11) on copper gold ores confirmed the results of Leaver and Woolf, in that, he similarly found that large amounts of copper (1%) in solution did not affect gold extraction, provided cyanide strength is maintained. Hedley states, that figures obtained by titrating copper bearing cyanide solutions with silver nitrate using KI as an indicator does not give a true measure of the free cyanide, in that it titrates part of the cyanide tied up by the copper cyanide complexes. He suggests that consistently high gold extraction can be obtained by maintaining the ratio of total cyanide to copper at 4 to 1.

However, the writers contend that the amount of cyanide titratable from the dissociation of the copper cyanide complexes is negligible, because of the high dissociation constant for the complex $Cu(CN)_3^{2-}$ ($K=5.0\times10^{-28}$). The decrease in the dissolution of gold should not be attributed to lack of free cyanide, because of incorrect figures obtained by titrating, but rather to the direct effect of copper on gold.

Leaver and Woolf (47) carried out an investigation on cyanide extraction of gold in arsenic and antimony compounds. They prepared artificial compounds and from

the cyanidation tests obtained the following results:

1. Direct cyanide treatment recovered nearly all of the gold in artificial iron-arsenic sulphide. Many natural arsenical pyrites similarly give high dissolution of gold by cyanide, indicating that the gold is present in a mechanical mixture and is exposed by fine grinding to the dissolving action of cyanide. However, there are instances in which the gold seems to be in solid solution with the pyrite and does not respond to direct cyanide recovery from the raw ore.
2. The gold compounded with ferric arsenate gave 80% extraction by direct cyanide treatment, 72% after roasting at 450°C and only 33.3% at 650°C. Lack of sulfur during the roast tends to prevent the formation of volatile arsenates and instead non volatile arsenates are formed which may lock up the gold against dissolution by cyanide. The addition of pyrite during roasting raises the recovery to 90%.
3. Calcium arsenate seems favorable for the dissolution of gold by direct cyanidation.
4. In the direct cyanide treatment of antimony compounds both iron antimony sulphide and ferric antimonate caused low extraction of gold with a high cyanide consumption.

5. Tests to determine whether poor extraction in direct cyanidation of certain arsenic and antimony ores could be attributed to the reprecipitation of gold, as carbon has been known to cause, gave no evidence to support this reaction.

An experimental study of the influence of pyrrhotite on cyanidation by Leblanc (44) revealed the following interesting points:

1. Effect of time of contact:
S^{--}, SO_4^{--}, CN^-, O_2 and CaO decrease with time,
$S_2O_3^{--}$, SCN^-, $Fe(CN)_6^{---}$ increased with time,
SO_3^{--} , little change,
pH decreased almost linearly.
2. Effect of concentration of NaCN:
S^{--}, $SO_4^{--}SCN^-$ increased with increase in concentration,
SO_3^{--}, O_2 irregular results,
Some CN^- going to CNO^-,
Loss of CaO greatest with small concentrations NaCN,
CaO loss decreased with increase in concentration,
pH followed the loss of lime,
3. CaO varied:
SCN^- and SO_4^{--} increased with increase in CaO,
$Fe(CN)_6^{----}$ and (CN^- loss) decreased at first, then constant,
$S_2O_3^{--}$ decreased.
4. Different compounds of pyrrhotite:
Of the two types investigated, Fe_{16} S_{17} and Fe_4S_5, Fe_4S_5

was found to be more active in the formation of S^{--}, SO_3^{--}, $S_2O_3^{--}$, CNS^-, $Fe(CN)_6^{----}$ and gave a larger decrease in CN^- and O_2.

5. Varying Pulp Density:

SO_4^{--} and total S increased with decrease in pulp density,
SO_3^{--} increased with decrease in pulp density,
CN^- loss increased with decrease in pulp density,
CNS^-, $Fe(CN)_6^{----}$, $S_2O_3^{--}$ constant.

From the investigational work carried out on the various minerals of copper, zinc, arsenic, antimony and iron, it is apparent that these minerals in general present special difficulties in cyanidation, because of the large cyanide consumption and decreased dissolution of gold in their presence.

7. Electrochemical Reaction

In the dissolution and precipitation of gold in alkaline cyanide solutions it seems probable that the various reactions are determined, as to their order and intensity, by the relative position of the elements concerned in the electro-chemical series.

Such a series for the metals in pure aqueous solutions of their salts is given in Table 1 (26).

Simply the table indicates that when two metals are in contact, the metal below accelerates the solution of the metal above it and is itself protected from dissolution by the latter. Or a metal tends to

precipitate from solution another metal which is below it and replace it in solution.

Table 1 Electrode Potentials at 25°C. Metal Ion at Unit Activity. Potentials Created by the Oxidation of a Metal

Electrode	Electrode Reaction	Potential
Al; Al^{+++}	$Al = Al^{+++} + 3(-)$	+ 1.70
Zn; Zn^{++}	$Zn = Zn^{++} + 2(-)$	+ 0.762
Fe; Fe^{++}	$Fe = Fe^{++} + 2(-)$	+ 0.441
Pb; Pb^{++}	$Pb = Pb^{++} + 2(-)$	+ 0.126
H_2; H^{+}	$H_2 = 2H^{+} + 2(-)$	0.000
Cu; Cu^{++}	$Cu = Cu^{++} + 2(-)$	-0.345
Ag; Ag^{+}	$Ag = Ag^{+} + (-)$	- 0.798
Hg; Hg_2^{++}	$2Hg = Hg_2^{++} + 2(-)$	- 0.799
Au; Au^{+}	$Au = Au^{+} + (-)$	- 1.68

But the series given in Table 1, (26), cannot be applied directly to the study of metals dissolved in mill solutions because the electrode potentials are different. The order of the metals in the electrochemical series depends not only on the nature of the elements themselves, but also on the chemical composition of the solution in which they are placed, its degree of concentration, its temperature, and in the case of gases, on the pressure. Unless all these conditions are taken into account, inference drawn from the electro-

chemical series in studying precipitation and dissolution phenomena are likely to prove more misleading than useful.

There are three principal reasons for these abnormalities in electrode potential and position (34):

1. The mill solutions are far more dilute than 1N (unit activity) in all dissolved constituents. A 1N solution of NaCN would contain 98 pounds of NaCN per ton.
2. The CN^- and OH^- concentration are interdependent.
3. Certain common metals (lead and aluminum) do not form complex cyanides and the metals that do form complex cyanides show marked differences in the stability of the complex ion.

Reynolds (26), in an application of basic electrochemical theory, theory of free energy of chemical reactions and dissociations constants of complex ions, to the most probable reactions occurring in mill solutions, has calculated the metal potentials. These along with determined potentials, are given in Table 2, (26).

The lead potential is important because of the universal use of lead as a precipitation accelerator, and it is unfortunate that it is not known. However, the author has placed it along with aluminum in the most probable position in the table.

Table 2(26) Electrode Potentials at 25°C. Metals in Equilibrium with a Solution in Which the Complex Cyanide or Complex Hydroxyl Ion and the CN^- or OH^- Ion are at Unit Activity

	Calculated	Measured
$Al + 4OH^- = Al(OH)_4^{1-} + 3(-)$	?	?
$Fe + 6CN^- = Fe(CN)_6^{4-} + 2(-)$	+1.53	?
$Zn + 4CN^- = Zn(CN)_4^{2-} + 2(-)$	+1.26	+1.26
$Zn + 4OH^- = Zn(OH)_4^{2-} + 2(-)$	+1.22	?
$Cu + 3CN^- = Cu(CN)_3^{2-} + (-)$	+1.09	?
$Pb + 3OH^- = Pb(OH)_3^{1-} + 2(-)$	?	?
$Au + 2CN^- = Au(CN)_2^{1-} + (-)$	+0.58	+0.536
$Ag + 2CN^- = Ag(CN)_2^{1-} + (-)$	+0.44	+0.418
$Hg + 4CN^- = Hg(CN)_4^{2-} + 2(-)$	+0.42	+0.37

Any wide variation from normal, in CN^-, OH^- and metal concentration may result in some transportation of the metals in the series.

An interesting illustration of the change in electrode potentials with variation of concentration of cyanide solutions is given in Table 3. The results are taken from an investigation carried out by Christy (45) in 1896-1899. The relative values show the wide variation in electrode potentials with cyanide concentration, resulting in some cases in an actual transportation of the positions of the metals in the series. Comparing Christy's results (Table 3) for a 0.065%

cyanide solution with those given by Reynolds (Table 2) one finds the same order of electrode potentials with the exception of iron. This is probably due to the fact that in calculating the electrode potentials it is assumed that all the metals are in their "active state".

Table 3 Electromotive Force of Metals in Cyanide of Potassium Solution

	Cyanide Concentration				
	6.5	0.65	0.065	0.0065	0.00065
Zinc	+0.945	+0.870	+0.775	+0.415	+0.385
Copper	+0.930	+0.680	+0.430	-0.050	-0.250
Gold	+0.420	+0.265	+0.090	-0.340	-0.450
Silver	+0.340	+0.195	+0.055	-0.310	-0.420
Lead	+0.200	+0.160	+0.110	+0.070	-0.050
Mercury	+0.150	+0.050	+0.040	-0.190	-0.590
Iron	-0.030	-0.090	-0.120	-0.130	-0.140

If any of the metals exhibit the complex phenomenon known as "passivity", the position of such metals, in the potential series, could only be determined by experiment. When a metal is in the passive condition it is shifted to a lower position in the electrochemical series, that is, it becomes more noble. This appears to be what has taken place when Christy determined the electrode potential of iron. Moreover, of the metals under discussion, only one, iron, normally becomes passive.

The above discussion has its principal application

in the precipitation of gold from alkaline cyanide solution, as ordinarily the introduction of metals into the cyanide solution is limited to zinc as a precipitant and lead as an accelerator, with minor instances of copper and mercury being present in the ore in the metallic state.

If a study of the dissolution phenomena with respect to electrode potentials is to be made, it is apparent that an electrochemical series is required of the different minerals found in the cyanidation of precious metal ores.

With this in mind Christy (45) in 1896 determined the electromotive force of various metals and minerals in different cyanide concentrations. The electromotive force of the common minerals are listed in Table 4.

Table 4 Electromotive Force of Metals and Minerals in Cyanide Solutions 1896

	Cyanide Concentrations %			
	6.5 Volts	0.65 Volts	0.065 Volts	0.0065 Volts
Aluminum	+0.99	+0.90	+0.76	+0.40
Zinc, Commercial	-----	+0.77	+0.59	+0.39
Copper	+0.81	+0.62	+0.37	+0.16
Bornite	+0.45	+0.25	-0.16	-----
Gold	+0.37	+0.23	+0.09	-0.38
Silver	+0.33	+0.15	-0.05	-0.36
Chalcocite	+0.29 (?)	+0.25	+0.05	-0.44

Table 4 continued:
Electromotive Force of Metals and Minerals in Cyanide Solutions 1896

	Cyanide Concentrations %			
	6.5 Volts	0.65 Volts	0.065 Volts	0.0065 Volts
Lead	+0.13	+0.05	+0.01	-----
Antimony	+0.06	+0.03	-0.03	-----
Arsenic	+0.04	-0.05	-0.21	-----
Niccolite	-0.11	-0.17	-0.44	-----
Iron	-0.17	-0.24	-0.24	-----
Chalcopyrite	-0.20	-0.34	-0.44	-----
Pyrite	-0.28	-0.42	-0.48	-----
Galena	-0.28	-0.48	-0.56	-----
Argentite	-0.28	-0.56	-0.55 (?)	-----
Arsenopyrite	-0.40	-0.45	-0.54	-----
Cuprite	-0.43	-0.55	-0.57	-----
Stephanite	-0.54	-0.55	-0.52 (?)	-----
Stibnite	-0.56	-0.56	-0.56	-----

Although, in the case of some of the minerals the values are questionable because of their high electrical resistance, the results are important in that they indicate the relative affinities of the minerals for cyanide solutions. They show, for instance, that not all copper minerals have a strong tendency to go into solution. Pure chalcopyrite has hardly more reaction than pure pyrite, while bornite and chalcocite have a very decided

tendency to go into solution. Cuprite is also apparently very little acted on, although to quote Christy, "This may be due to its high resistance rather than to a lack of tendency to dissolve." It is plain however that pure chalcopyrite, galena, argentite, arsenopyrite, stephanite and stibnite, when free from their oxidation products, are apparently little acted on by cyanide solutions.

Since the fundamental characteristics of any electromotive series is that a metal will displace from solution any metal below it in the series or that the metal below accelerates the dissolution of the metal above it, it is interesting to note that of the minerals investigated Table (4) only bornite would tend to prevent the dissolution of gold, whereas pyrite, chalcopyrite, galena being below gold in the series would tend to aid in its dissolution.

An investigation carried out by Plaksin (46), on the rate of dissolution of gold in the cyanide process and the effect of contact with minerals and metal surfaces on this rate, would seem to bear out the above point. Cyaniding gold leaf with a mineral in a 0.3% KCN solution produced the following results:

	% Recovery
Au alone	10.28
Au + Quartz	40.33
Au + Limonite	74.83
Au + Chalcopyrite	73.81
Au + Galena	67.15
Au + Pyrite	91.33

The results indicate that the presence of a mineral increases the dissolution rate of gold, a possible explanation being that the particles of metallic gold in contact with the minerals form small galvanic cells of such an order that the dissolution of gold is aided, as predicted by the relative positions in Table 4.

To date, the study of the dissolution and precipitation of gold with respect to electrode potentials is limited, in that little work has been done on minerals in cyanide solutions, however, the work carried out has pointed the way for further investigation.

II PRECIPITATION

A. MECHANISM

The precipitation of gold from an alkaline cyanide solution is accomplished by the reduction of Au^+ ion by a metal that can yield an electron to the Au^+ ion with the resultant production of Au^0 metal.

In the precipitation chamber three reactions proceed simultaneously (34).

$$Au(CN)_2^- = Au^+ + 2CN^- \ldots\ldots\ldots\ldots(1)$$

$$Au^+ + R^0 = Au^0 + R^+ \quad \ldots\ldots\ldots\ldots(2)$$

$$R^+ + ZCN = R(CN)_z^{n-} \quad \ldots\ldots\ldots\ldots(3)$$

Equation (1) and (3) are reversible and proceed to the equilibria specified by the dissociation constants of $Au(CN)_2^-$ and $R(CN)_z^{n-}$. Equation (2) proceeds to completion to the right, the prerequisite being that R^0 must be above monovalent gold in the galvanic series for the solution.

Combined, the above equations give the general precipitation equation:

$$Au(CN)_2^- + R^0 = Au^0 + R(CN)_z^{n-}$$

The function of the precipitant is solely to yield up an electron to the aurous ion produced by the dissociation of $Au(CN)_2^-$. In other words, if aurocyanide ion did not dissociate, no precipitation of gold would occur.

As previously stated the prerequisite of a precipitant for gold is essentially one which is above monovalent gold in the galvanic series for the solution. These series have been discussed in some detail in the section "Electrochemical Reaction" and will not be repeated here. From the series given by Reynolds it is

apparent that any one of the metals, aluminum, zinc, iron, copper or lead would fill the theoretical requirements of a precipitant for gold. However, operating conditions limit the application of these metals essentially to that of zinc and aluminum.

B. METHODS OF PRECIPITATION

1. Zinc

There are several methods of precipitating gold and silver from pregnant cyanide solution. The most widely used is zinc, either in the form of dust or shavings. The reaction between zinc and the aurocyanide may be expressed theoretically by the equation:

$$Zn + 2KAu(CN)_2 = K_2Zn(CN)_4 + 2Au$$

The equilibrium constant of this reaction calculated from the free energy change of the reaction is $K = 10^{18.6}$ (26) or in other words the reaction favors the precipitation of substantially all the gold in solution.

As the precipitation of gold by zinc is usually performed in the presence of free cyanide, some investigators prefer to represent the precipitation by the following equation:

$$KAu(CN)_2 + 2KCN + Zn + H_2O = K_2Zn(CN)_4 + Au + H + KOH$$

and when no free cyanide is present, by the equation:

$$KAu(CN)_2 + Zn + H_2O = Zn(CN)_2 + Au + H + KOH$$

In addition to the above reactions it is quite probable that the further reaction occurs:

$Zn + 4KCN + 2H_2O = K_2Zn(CN)_4 + H_2 + 2KOH$

Whatever be the exact terms of the reaction, zinc replaces the precious metal in the solution and there is a tendency for this zinc to accumulate in the mill solution after repeated use. It is in precipitation that the double cyanide $K_2Zn(CN)_4$ is formed which plays an important part in cyanide regeneration.

On considering the dissolution and precipitation reactions for gold one finds they are diametrically opposed in their action and effect. It has been shown that the dissolution of gold cannot proceed in the absence of oxygen. Therefore, the removal of dissolved oxygen from the gold solutions, prior to the introduction of the zinc dust, is essential if the re-dissolution of the gold in the precipitation chamber is to be prevented. Today, this is accomplished by placing the solution under vacuum, which removes practically all the oxygen. Prior to the development of vacuum-deoxygenation, oxygen was removed from solution by:

1. combination with excess zinc to form a series of hydrous zinc compounds known as white precipitate.
2. combination with atomic hydrogen, generated by corrosion of excess zinc, to form water. Thus modern vacuum deoxygenation results in the marked reduction of zinc consumption.

The theory of free energy change gives no idea of how long it would take the precipitation reaction to reach equilibrium. Aurocyanide, being a complex ion, is a very stable and one might anticipate that it would take an appreciable length of time to reach equilibrium. Normally the reaction is not complete in the flow time through the press and an accelerator must be used. MacArthur, when he patented his process advised coating the zinc, (which he used in the form of shavings), with a lead film to increase the activity of precipitation. Later this was modified by the addition of soluble lead (Pb^{++} ion) consisting of a drip of either lead acetate or lead nitrate. The mechanism by which this acceleration is obtained is not completely understood but several theories have been postulated. Many authorities claim the function of the Pb^{++} ion is to gorm a Zn-Pb couple and that this couple increases the rate of gold precipitation. That such a couple does form is possible, the reaction being:

$$Zn + Pb^{++} = Zn^{++} + Pb$$

However, this still does not explain why the lead accelerates the precipitation. Another theory (34) is that the Pb^{++} acts as a catalyst to increase the rate of the zinc-aurocyanide reaction. This may be substantiated in the near future when the mechanism of the catalyst has been unfolded, in view of the large

amount of research being carried out in this direction in the field of chemistry.

Although zinc is used universally as a precipitant it has disadvantages. As a result of its use Zn^{++} ion is produced. Zn^{++} ion unites with $4CN^-$ ions to form $Zn(CN)_4^{2-}$ and this ties up a large amount of expensive cyanide. Some of the zinc ions also combine with the carbonate ions in solution forming solid basic zinc carbonate. This must be removed in subsequent refining. A precipitant accelerator soluble lead salt must be used with zinc dust. An end result of the use of this accelerator is Pb metal which must also be removed in refining.

2. Aluminum

Aluminum dust has been used for precipitating gold from cyanide solutions. According to Moldenhauer who patented the process in 1893, the following reactions take place:

$$6NaAu(CN)_2 + 6NaOH + 2Al = 6Au + 12NaCN + 2Al(OH)_3$$

the aluminum hydroxide at once dissolving in the excess of caustic to form sodium aluminate:

$$2Al(OH)_3 + 2NaOH = Na_2Al_2O_4 + 4H_2O$$

The fact that aluminum does not replace the precious metals in the cyanogen compound, renders necessary the presence of caustic soda in the solution.

One point vital to the practical application of aluminum is the absence of lime at the time of precipitation, as it decomposes the sodium aluminate to form insoluble calcium aluminate;

$$Na_2Al_2O_4 + Ca(OH)_2 = CaAl_2O_4 + 2NaOH$$

This deposits in the press with the precipitate, making a large bulk of low grade product which it is almost impossible to smelt.

Aluminum has been used with success at the Deloro Smelter, Canada, and at the O'Brien Mine in Cobalt in treating silver ores containing antimony and arsenic. The equation already given shows that the whole of the cyanogen combined with silver is regenerated in the form of alkaline cyanide. This theoretical increase in cyanide strength was borne out by actual titrations before and after precipitation.

The method of working is somewhat similar to that for zinc dust but the action is slower in practice, because, although for an excess of aluminum dust the reaction is rapid, economic considerations necessitate the use of smaller amounts and a proportionately longer precipitation time.

3. Charcoal

Charcoal has also been used for precipitating gold from cyanide solutions. Originally the solution was passed through barrels packed with charcoal which were

later burned and the ash melted down with fluxes. Later methods of application required that the charcoal be ground to a fine powder and agitated with the solutions with subsequent filtering and smelting of the ash in the usual way.

A more recent innovation in the application of charcoal as a precipitant, is a process devised by Chapman (21) known as "A cyanide process based on the simultaneous dissolution and adsorption of gold." The ore along with the cyanide, charcoal and lime is ground in a ball mill with classification, then thickened, agitated and fed to flotation machines. The charcoal with the adsorbed gold is floated off and treated for gold recovery. The tails are thickened, with the overflow going back to the flotation cells and the underflow going to the mill pond. Possible applications of the process are:

1. Ore and tailings containing large amounts of finely divided constituents of such character that the settling rate of the solids is too slow for practical countercurrent decantation operations. Ores of this class also present difficulties to filtering.
2. Graphite gold ores in which the graphite acts in a similar manner as the adsorbing charcoal. (Graphite has been rendered inactive in cyanidation by the addition of small amounts of kerosene which coats the

graphite).

3. Certain mixed ores with part of the gold intimately associated in the sulphides, the refractory gold being floated with the charcoal.

4. Low grade ores and tailings that may be economically treated because of the simplicity of the method.

The author claims the advantage, that by the law of mass action, since the gold is removed from solution as rapidly as dissolved, the avidity of the solution for gold is maintained at a maximum, thus insuring the maximum speed of dissolution. This advantage appears doubtful when it is considered that the amount of actual cyanide tied up by gold is practically negligible.

The process requires a low cyanide strength in that the solutions at the end of one cycle are discarded to tailings. In this respect its application, to the dissolution of copper ores in a process described by Clarke (13) requiring weak cyanide solutions, might be used to considerable advantage.

4. Electrolytic

Since electricity has been used successfully for many years in gold and silver electroplating, it would seem that this method would be a simple and practical method of precipitating gold from the cyanide solutions. However, the principal difficulty is one that cannot be obviated, that is, the high specific resistance of the

dilute solutions that must be used. With cyanide solutions of 0.05% free cyanide and perhaps 0.001% of gold, or less, the resistances are enormous. The high resistance of the solution has been met by using an increased surface of anode and cathode and by artificial circulation, but this offsets the cheapness and simplicity of the method.

Electrolytic precipitation has been used commercially on the Rand for precipitating weak, low grade solutions. It was known as the Siemens-Halske process and consisted of anodes of sheet iron wrapped in burlap. The cathodes were sheets of lead bunched together. The process was not altogether a success due to uncertainty in results and cost of handling.

Electrolytic methods of precipitation are used in the analytical laboratory as a convenient and accurate method of analysis.

C. FACTORS AFFECTING PRECIPITATION

Whatever method of precipitation is used, it is of great importance that the solution should be clear and free from suspended matter. It is therefore, almost always advisable to clarify it by filtration before precipitation.

As previously mentioned the addition of lead salts in precipitation is necessary as an accelerator.

However, improper application of lead salts may lead to trouble in precipitation. The addition of too much lead may cause an excessive zinc consumption and a low grade precipitate which is difficult to refine. Further an actual retardation in the precipitation may result.

The elimination of all dissolved oxygen during precipitation is of utmost importance as an air leak into the press feed after dearation, may cause re-dissolution of the gold at a rapid rate. Careful supervision at all times is required for good precipitation.

Reynolds (20) in a discussion of the effects of dearation on precipitation of cyanide solutions attributes the rapid build up of pressure in precipitation presses generally to two causes: the first and most usual, faulty clarification and second, the improper use of lead salts. In some cases however, the clarified solutions may be clear and brilliant, yet slimy difficult filtered precipitates are obtained regardless of the quantity of lead salts fed, and where it is added. Standard practice is to clarify, dearate, add zinc dust and precipitate. Deaeration after clarification may be the cause of trouble in succeeding precipitation. If the solutions contain impurities that go out of solution upon deaeration double deaeration would be required to avoid rapid pressure built up in the precipitation press.

The first deaeration would be ahead of clarification and the second between clarification and precipitation, in the usual place. If lead forms insoluble compounds it should be added prior to first deaeration, otherwise just ahead of the precipitation press. Any insoluble compounds thrown down in the first deaeration would be caught on the clarifier leaves and worked off with the ore slime. From this point the usual clarification-precipitation process is carried out.

An investigation of some of the various factors affecting precipitation was carried out by Leblanc (18). Working with an artificially prepared gold solution and conditions simulating actual plant practice as close as possible, he arrived at the following general conclusions:

1. Best precipitation is obtained when the free cyanide content is 0.31 pounds per ton.
2. The pH, or total alkalinity, of a solution has a marked influence on precipitation, a pH of about 11.6 giving maximum recovery.
3. The quantity of lime giving the best recovery is about 0.56 pounds per ton.
4. Sulphide, sulphite, sulphate, thiosulphate; ferrocyanide and zinc cyanide when present in the solution lower the recovery.

5. A lead salt in small amounts improves precipitation, when an excess is present however precipitation is retarded.

6. The higher the gold content in solution the better the recovery, all other things being equal.

7. The amount of zinc added to the solution is important. A molecular ratio of zinc to gold, if less than 100 to 1, lowers the recovery.

8. The recovery is lowered if the temperature of the solution is below 20°C.

III CYANIDE REGENERATION

A. NATURAL

Cyanide regeneration, as the name implies, is the reformation of cyanide due to the action of some chemical in the solution. According to Hamilton (35) this regeneration may take place from two causes. Firstly, precipitation of zinc by the soluble sulphides formed during contact of the solution with the ore, as follows:

$K_2S + K_2Zn(CN)_4 = ZnS + 4KCN$

Secondly, the reaction of free alkali on the double cyanide with the formation of an alkaline zincate and free cyanide:

$K_2Zn(CN)_4 + 4KOH = K_2ZnO_2 + 4KCN + 2H_2O$

In the operation of cyanide plants many metallurgists have observed that when the lime content is raised from just protective up to 0.10 -- 0.13% CaO,

a saving in cyanide is observed. This would tend to indicate that part of the combined cyanide has been decomposed, thus liberating free cyanide from the double cyanide $K_2Zn(CN)_4$.

$K_2Zn(CN)_4 + 2Ca(OH)_2 = 2KCN + Ca(CN)_2 + CaZnO_2 + 2H_2O$

The formation of the insoluble calcium zincate renders the reaction non reversible.

B. ARTIFICIAL

The problem of artificial regeneration of cyanide has received considerable attention by investigators. Cross (43) patented a process based on the principle of precipitating zinc as a sulphide by the addition of sodium sulphide,

$K_2Zn(CN)_4 + Na_2S = ZnS + 2KCN + 2NaCN$

However, the process was not much of a success due to the presence of sodium zincate which reacted with the sodium sulphide to form sodium hydroxide,

$Na_2ZnO_2 + Na_2S + H_2O = ZnS + 4NaOH$

The hydroxide accumulating in the precipitation chamber involved an additional zinc consumption.

Several other methods of regenerating cyanide solutions have been proposed, chiefly based on the principle of precipitating the base metals in acids. Halferdahl (22), from a survey of available literature with regard to regeneration of cyanide from cuprifirous cyanide-plant precipitates, found that:

1. Electrolysis of original-ore cyanide solutions has not been successful in precipitating copper and regenerating the cyanide.
2. Regeneration by acidification of residual plant solution originally proposed by MacArthur, will recover about 50% of the bound cyanide, depending on the character of the ore.

Acidification is accomplished with sulfur dioxide or sulphuric acid. Removal of liberated hydrogen cyanide is made possible by distillation under vacuum or by passing air through the solution. The resulting vapors are passed through alkaline solutions to fix the HCN.

Leaver and Woolf (12), working with copper bearing solutions, precipitated the copper with the regeneration of free cyanide by the use of sodium sulfide in an acid solution. However, cyanide loss as cyanates cannot be recovered by this process. The cyanide regenerated has the same dissolving efficacy as the fresh cyanide. Satisfactory tests on difficult ores were performed and gave concordant results with the preliminary investigations.

A practical application of cyanide regeneration, as put into use by the Compania Beneficiadora de Packucca, Mexico, is described by Lawr (23). The solutions are acidified by contact with sulfur dioxide and then transferred into closed tanks. Air is brought into contact

with the solutions and leaving the tank, charged with HCN, is passed through an alkaline solution which fixes the HCN.

IV SUMMARY

Investigational work in general falls into one of two classes, either pure research or economic investigations. The former establishes the chemical reactions involved, their products and influencing factors, and, has its application in furthering general knowledge of the process or problem as a whole. The latter strives to solve individual problems, resulting in a compilation of numerous investigational results that cannot be correlated or in many instances interpreted for the problem in question. Moreover, since the extent of the test work is guided by economical considerations, only a restricted knowledge of the problem is obtained.

The foregoing study of the cyanide process, in the light of past work has shown that the greater portion of investigational results belongs to the latter class. The need of further studies, to give a more complete chemical and electrochemical picture of the process, becomes apparent. In particular, such work should be directed towards detailed studies of the effects of base metals, alkalinity, oxygen and artificial oxidizers, and addition reagents.

CYANIDATION
and the
COPPER MINERALS

CYANIDATION AND THE COPPER MINERALS

Table of Contents

I The Copper Minerals

II Copper Solubility and Solubility Factors

A Mechanisms

- (1) Native Copper
- (2) The Copper Salts

B Solubility Factors
- (1) Oxygen Content
- (2) Hydrogen Ion Concentration
- (3) Cyanide Strength
- (4) Temperature
- (5) Pressure
- (6) Presence of "Foreign" Substances
  - (a) pH
  - (b) Electrochemical Effect
  - (c) Common Ion
  - (d) Salt Effect
- (7) Time of Contact
- (8) Catalytic Action
- (9) Physical Condition of Minerals

C Previous Experimental Work

- (1) Leaver and Woolf
- (2) Christy

III Methods of Rendering Copper Inactive

A Removal

- (1) Leaching
- (2) Flotation

B Control

- (1) Chemical
  - (a) Precipitation
  - (b) Common Ion
  - (c) Weakly Ionized Compounds
  - (d) Complex Ions
  - (e) Change of Valence

- (f) pH
- (g) Oxygen
- (h) Cyanide Strength
- (i) Temperature
- (j) Electrochemical
- (k) Catalytic Effect
- (l) Selective Adsorption
- (m) Mineral Surface Coating

(2) Physical

- (a) Time of Contact
- (b) Grain Size

C Cyanide Regneration

- (1) Electrolysis
- (2) Precipitation
- (3) Distillation

CYANIDATION AND THE COPPER MINERALS

It is shown in the preceding discussion that copper minerals are a cyanicide in that they form complex copper cyanide ions and rob the cyanide solution of the essential dissolving agents. It is now pertinent that these minerals, their properties by which they become a cyanicide, the factors affecting these properties, and methods by which these factors may be controlled, be examined in detail. This examination is under the following headings:

I The Copper Minerals,

II The Solubility and Factors Affecting the Solubility of Copper Minerals in Cyanide Solution,

III Methods of Rendering Copper Inactive to Cyanide Solution.

I THE COPPER MINERALS

The main copper minerals may be divided into three classes; native copper, oxides and oxygen salts of copper, and the copper sulphides. Dana (53) recognizes the following to be the most prominent of these minerals.

Native Copper	Oxides and Oxygen Salts	Sulphides
Cu	Cuprite - Cu_2O	Chalcocite Cu_2S
	Malachite - $CuCO_3.Cu(OH)_2$	Covellite - CuS
	Azurite - $2CuCO_3.Cu(OH)_2$	Bornite - Cu_5FeS_4
	Brochantite - $CuSO_4.3Cu(OH)_2$	Chalcopyrite $CuFeS_2$
	Chalcanthite - $CuSO_45H_2O$	Tetrahedrite - $3Cu_2S.Sb_2S_3$
	Atacamite - $CuCl_2.3Cu(OH)_2$	Enargite - $3Cu_2.As_2S_5$
	Chrysocolla - $CuSiO_3.2H_2O$	Stannite - $Cu_2S.FeS.SnS_2$
		Tennantite - $3Cu_2S.As_2S_3$

II THE SOLUBILITY AND FACTORS AFFECTING THE SOLUBILITY OF COPPER MINERALS IN CYANIDE SOL'N.

This topic is subdivided into the following divisions for clarity:

(A) Mechanisms of Dissolution

(B) Solubility Factors

(C) Previous Experimental Worl

(A) MECHANISMS OF DISSOLUTION

This subject is discussed under two sections as each section embraces a different mode of dissolution.

(1) Native Copper

The accepted equations (26) for the dissolution of native copper have been stated and the thermodynamic possibilities explored. These equations are repeated and subjected to further analysis:

(i) Elsner equation for oxygen bearing solutions,

$$4Cu + 12NaCN + 2H_2O + O_2 = 4Na_2Cu(CN)_3 + 4NaOH$$

$$K = 10^{103.5}$$

(ii) Janin equation for oxygen free solutions,

$$2Cu + 6NaCN + 2H_2O = 2Na_2Cu(CN)_3 + 2NaOH + H_2$$

$$K = 10^{8.9}$$

The type of reaction in both cases is one of oxidation-reduction with the formation of a stable complex ion aiding in the ease of copper oxidation. This is illustrated as follows:

(i) expressed as an ionic equation

$$4Cu + 12Na^{+} + 12CN^{-} + O_2 + 2H_2O = 8Na^{+} + 4Cu(CN)_3^{=} + 4Na^{+} + 4OH^{-}$$

The Na^{+} ions are common to each side of the equation and may be disregarded.

$$4Cu + 12CN^{-} + O_2 + 2H_2O = 4Cu(CN)_3^{=} + 2OH^{-}$$

the native copper is oxidized and the O_2 and H_2O reduced.

$4Cu + 12CN^{-} = 4Cu(CN)_3^{=} + 4e$ -oxidation

$O_2 + 2H_2O + 4e = 4OH^{-}$ -reduction

(ii) $2Cu + 6Na^{+} + 6CN^{-} + 2H_2O = 4Na^{+} + 2Cu(CN)_3^{=} + 2Na^{+} + 2OH^{-} + H_2$

dropping the Na^{+} ions,

$2Cu + 6CN^{-} + 2H_2O = 2Cu(CN)_3^{=} + 2OH^{-} + H_2$

$2Cu + 6CN^{-} = 2Cu(CN)_3^{=} + 2e$ -oxidation

$2H_2O + 2e = H_2 + 2OH^{-}$ -reduction

An examination of the "strength" of the oxidizing agents shows why the oxygen bearing cyanide solution is the better solvent for copper. This "strength" is best expressed by oxidation potentials. If the oxidation potential value is large and positive the agent is a good oxidizer, while if the oxidation potential value is negative and large the agent is a poor oxidizer.

$O_2 + H_2O + 4e = 4OH^-$ $E^\circ = + 0.401$ (54)

$2H_2O + 2e = H_2 + 2OH^-$ $E^\circ = - 0.828$ (54)

Thus it is seen that the oxygen bearing solution is a much more efficient solvent than the oxygen free solution.

A study of the oxidation potentials also shows the part played by the complex ion formation.

$Cu = Cu^{++} + 2e$ $E_o = -0.34$ (54)

This means that the copper is hard to oxidize. When cyanide is added,

$Cu + 3CN^- = Cu(CN)_3^{=} + e$ $E_o = + 1.09$ (55)

The copper is now readily oxidized, so much so that the oxygen free solution, a very poor oxidizer, may do so.

(2) The Copper Salts

The solubility of the copper salts in cyanide solution is dependent upon the ease by which they go into solution as simple ions. Once the copper ion is present in solution it forms the stable copper complex with the cyanide ions in the following manner:

(i) Univalent copper

$Cu^+ + 3CN^- = Cu(CN)_3^{=}$

(ii) Divalent copper

$Cu^{++} + 2CN^- = Cu(CN)_2$

$2Cu(CN)_2 = 2CuCN + C_2N_2$ (cyanogen)

$CuCN + 2CN^- = Cu(CN)_3^{=}$

(it is probable in cyanide solution that the cupric ion

is reduced to the cuprous by some other means, say the ferrous ions, as cyanogen has not been reported in or about the cyanide solutions during dissolution).

The ease, with which slightly soluble copper salts go into solution, depends on their solubility product, the stability of the complex ions formed, and the concentrations of the ions present in solution. The simple sulphides may be considered as typical. The solubility products of the sulphides are very low. The Ks.p. for CuS is 2.5×10^{-41} and for Cu_2S is 2×10^{-47} (59). The instability constant for $Cu(CN)_3^{=}$ is 5×10^{-28}, not so low as the Ks.p. of the sulphides. Normally, then, the sulphides do not ionize sufficiently to produce high enough concentrations of copper ions to exceed the instability constant of $Cu(CN)_3^{=}$. The complex ion is not formed and the sulphide does not dissolve. But if the sulphide ion concentration is kept very low the copper ion concentration may rise so that the K instab. is exceeded and the complex will be formed. Similarily if the cyanide ion concentration is high the necessary copper ion concentration will be reached resulting in the formation of the complex ion. Then the sulphide dissolves. This action may be clarified as follows:

$$\begin{array}{ll} Cu_2S = 2Cu^{+} + S^{=} & \qquad Ksp = 2 \times 10^{-47} \\ \qquad + 6\,CN^{-} & \\ \qquad // & \\ \quad 2Cu(CN)_3^{=} & \qquad \dfrac{(Cu^{+})(CN^{-})^3}{Cu(CN)_3^{=}} = K\ instab. = 5 \times 10^{-28} \end{array}$$

Low $S^{=}$ results in high (Cu^{+}) - K instab. exceeded - Sulphide dissolves

High (CN^{-}) with low (Cu^{+}) - K instab. exceeded - Sulphide dissolves

In cyanide solutions the sulphide ion concentration is kept low by oxidation to the sulphate, the sulphite, or the thiosulphate ion. Further the cyanide ion concentration is necessarily high for the dissolution of gold and silver. Thus the two factors result in the copper sulphides going into solution.

While the fundamental reactions for copper dissolution are recognized, one wonders what is the actual physical means by which the reactants combine. It has been proposed that the dissolution of gold is a heterogeneous reaction originating at the gold surface. It would seem logical that such is the case for native copper. But one becomes interested to learn if this holds true for the copper salts. Unfortunately no theorizing has been done with reference to this particular case. The complexity of the problem excludes it from a work of this nature.

Up to the present the possibility of the formation of complex ions other than $Cu(CN)_3^{=}$ has been tactfully ignored and all theoretical consideration has been limited to the tri-cyanide copper complex. Several writers have postulated the existence of the other

copper cyanide complex ions but there has been no definite proof, theoretical or otherwise. Hedley and Kentre (11) state "It is generally accepted that copper in cyanide solution can form complex ions such as $Cu(CN)_2^-$. $Cu(CN)_3^=$, and $Cu(CN)_4^{\equiv}$, although $Cu(CN)_3^=$ is considered the most likely of these." Field (64) on discussing formulae of double cyanides writes, "Those of copper are less definite, there being a number of these complex double cyanides according to the method of preparation. The formula most usually ascribed to the compound is CuCN.2KCN." Reynolds (26) considers only $Cu(CN)_3^=$. Latimer (56) lists only $Cu(CN)_2^-$, while Yoe (59) gives $Cu(CN)_3^=$. Thompson (65) states the probable complex ions present in cyanide plating baths are

"Major complex ion - $Cu(CN)_3^=$
Minor complex ions - $Cu(CN)_2^-$, $Cu(CN)_4^{\equiv}$."

An examination of the instability constants tends to show that, for cyanide solutions used in gold milling, the $Cu(CN)_3^=$ is the most likely ion. The following are the published values:

(1) $Cu(CN)_2^- = Cu^+ + 2CN^-; \quad \frac{(Cu^+)(CN^-)^2}{Cu(CN)_2^-} = 1 \times 10^{-16}$ (57)

(2) $Cu(CN)_3^= = Cu^+ + 3CN^-; \quad \frac{(Cu^+)(CN^-)^3}{Cu(CN)_3^=} = 5.0 \times 10^{-28}$ (26)

(3) $Cu(CN)_4^{\equiv} = Cu^{+} + 4CN^{-}$; $\frac{(Cu^{+})(CN^{-})^4}{Cu(CN)_4^{\equiv}} = 5.0 \times 10^{-28}$ (66)

Dividing (1) by (2) the following relationship is determined:

$$\frac{(Cu(CN)_3^{=}}{(Cu(CN)_2^{-}) x (CN^{-})} = 2.0 \times 10^{11}$$

$$\frac{(Cu(CN)_3^{=}}{(Cu(CN)_2^{-}} = 2.0 \times 10^{11} \times (CN^{-})$$

for 0.100% NaCN solution and 0.036% Cu ~~in~~ the (CN^{-}) concentration is 0.004 gm.mol/L (see Appendix (A)-Sec.B)

then $$\frac{(Cu(CN)_3^{=})}{(Cu(CN)_2^{-}} = 2.0 \times 10^{11} \times 0.004 = 8.0 \times 10^{8}$$

That means for the above solution the concentration of $Cu(CN)_3^{=}$ is 8.0×10^{8} times the concentration of $Cu(CN)_2^{-}$

By dividing (2) by (3)

$$\frac{(Cu(CN)_4^{\equiv})}{(CN^{-})(Cu(CN)_3^{=}} = 1$$

$$\frac{(Cu(CN)_4^{\equiv})}{(Cu(CN)_3^{=})} = 1 \times (CN-)$$

Similarily for the 0.100% NaCN solution and 0.036% Cu

$$\frac{Cu(CN)_4^{\equiv}}{Cu(CN)_3^{=}} = 1 \times 0.004$$

or under these conditions the $Cu(CN)_3^{=}$ concentration is 250 times as great as the $Cu(CN)_4^{\equiv}$ concentration.

So while it is a safe assumption to make that the tricyanide copper complex ion is by far the most

prevalent in gold extraction cyanide solutions, the possibilities of the existence of the other complex ions can not be over looked.

(B) SOLUBILITY FACTORS

From the foregoing study of dissolution mechanisms it becomes evident the oxygen content of the solution, the hydrogen ion concentration, and the cyanide strength are all factors in the rate and extent of copper dissolution.

(1) Oxygen Content

No experimental work has been done in determining the solubility of copper under conditions of varying oxygen availability. However, from the family similarity of copper and gold (52) and from the relative values of the reaction constants for oxygen free and oxygen bearing cyanide solutions it can be predicted that by increasing the oxygen content of the solution, providing sufficient quantities of the other reactants are present, the copper sulubility will increase.

(2) Hydrogen Ion Concentration

In the case of the hydrogen ion, the situation is more complex in that there are two conflicting tendencies. An increase of the hydrogen ion concentration would hasten the oxidation of the copper by decreasing the hydroxyl concentration and shifting the reaction equilibrium further to the right. However, the avail-

ability of the cyanide ions is inversely proportionate to the hydrogen ion concentration, as explained in the section on cyanidation and briefly repeated here:

$$\frac{(HCN)(OH^-)}{(CN^-)} = 7.2 \times 10^{-4}$$

$$(H^+)(OH^-) = 10^{-14}$$

Thus high hydrogen ion concentration would cut down the cyanide ion concentration and repress the complex copper ion formation. This action is probably much greater than the increased oxidizing action. Here, too, there is no experimental substantiating evidence.

(3) Cyanide Strength

Variation of cyanide strength will proportionately influence the copper solubility providing sufficient amounts of the other reactants are available to complete the reaction. A concentrated cyanide solution will give a high copper content. However, this is only true when there is no change in the percent hydrolysis of the cyanide ion. The following values are taken from results of a series of cycling tests performed by Hedley and Kentro (11).

NaCN %	Cu %
0.134	0.038
0.179	0.054
0.209	0.069
0.282	0.083
0.341	0.089
0.407	0.092

In the preceding discussion the mechanisms of dissolution and the pertinent factors have been considered only when the principal constituents are present and under one set of conditions, i.e. pressure and temperature. It is now advisable to study variations of conditions and introduction of "foreign" substances and their effect on copper solubility.

(4) Temperature

The effect of change of temperature on the dissolution of a salt in an aqueous solution is determined by whether the reaction is exothermic or endothermic, that is, whether heat is evolved or absorbed. If heat is absorbed, by Le Chatelier's principle, an increase of temperature will speed up the dissolution. However, the formation of the complex copper ions, which influences the copper salt solubility, is a reaction between ions and is greatly influenced by temperature. Meldrum and Glucker (71) give this empirical relationship, "A rise of 10°C in temperature approximately doubles the rate of a chemical reaction." The increase of reaction rate is due to the greater activity of the ions. From a table in Mellor's Treatise (50) it is noted that copper is twenty four times more soluble in a cyanide solution at 71°C than when the solution is at 15.6°C.

(5) Pressure

Variation of pressure affects the extent and rate of reaction if the formation of a gas is involved. Normally an increase of pressure retards the gas formation and the reaction is slowed down. However, in cyanidation, greater air pressure increases the concentration of oxygen (Henry's Law) and the reaction equilibrium is shifted further to the right. If an excess of cyanide be present, additional copper will dissolve.

(6) Presence of "Foreign" Substances

Here the word "foreign" refers to substances already in the cyanide solution, introduced by the ore and by operating conditions rather than intentional introduction. These are numerous and have complex effects on copper dissolution, while together the effect is confused and not subject to clear analysis. For this reason the discussion is very broad and limited to general considerations.

(a) Those substances that affect the pH or hydrogen ion concentration of the solution.

Under this category there are two types of substances. First are the minerals that hydrolyse, tending to make the solution either acidic or basic. The minerals that are salts of a strong acid and weak base acidify the solution while the minerals that are the salts of a weak acid and strong base make the solution basic. Generally

it has been found that gold ores tend to acidify the cyanide solution. Secondly are the dissolved gases, such as carbon dioxide, that form weak acids. The effects of hydrogen ion concentration change have been discussed previously.

(b) Minerals that influence dissolution electrochemically.

Various minerals in contact with each other and in cyanide solution may be considered as an electrochemical cell. The solution comprises the electrolyte and the minerals the electrodes. If a mineral in conjunction with the solution is electronegative to the copper mineral and the solution, the copper mineral will dissolve. This action is dependent on the difference in electric potentials, the concentration of the ions in solution, and the temperature. While no work has been done to substantiate this theory in cyanide solutions, the principle has been observed when the leaching of copper ores is performed.

(c) The Common ion.

The introduction of a salt, which ionizes to give an ion the same as that produced by the copper mineral, will effectively limit the copper solubility. As an example, if sufficient Na_2S is added to a solution of Cu^{++} and $S^{=}$ ions, CuS will precipitate out.

(d) The salt effect.

The solubility product principle does not hold when other salts are in solution to an excess of 0.3M (62). It is not necessary for the additional salts to produce any common ions. The solubility of the original salts are greater than can be predicted by the solubility of the salt.

(7) Time of Contact of the Cyanide Solution With the Copper Minerals.

Unless the dissolution of the copper minerals in a cyanide solution is instantaneous it is obvious that the time of mineral solution contact is a factor in the extent of copper mineral dissolution.

(8) Catalytic Action

The foregoing reactions may be influenced by the presence of catalysts. Prutton and Maron (72) define a catalyst as "any substance which influences the rate of chemical reaction but itself remains unchanged chemically." While the mechanism of catalysis is not clearly understood it is believed that the catalyst makes for a more intimate or less intimate association of the reactants. Thus reactions may be hastened or retarded. In the latter case the catalyst is known as a negative catalyst. This subject of catalysis has not been investigated with respect to dissolution of copper minerals in cyanide solution but the possibilities are

not to be overlooked.

(9) Physical Conditions of the Minerals

All previous discussion has been limited to a purely chemical reasoning which assumes that the mineral is readily available to solvent action. This is not necessarily so. The dissolution rate is a function of the particle size (63). Also the surface of the mineral may differ in composition from the bulk of the mineral. Further a mineral in the crystal form is less soluble than that of the amorphous state (67).

Summary of factors:

It is now desirable to present the factors affecting copper solubility in a summarized form.

(1) ph
(2) Oxygen content
(3) Cyanide strength
(4) Temperature
(5) Pressure
(6) Electrochemical effect
(7) The common ion
(8) The "salt" effect
(9) Time of contact
(10) Catalytic action
(11) Particle size and condition.

(6) PREVIOUS EXPERIMENTAL WORK

(1) Leaver and Woolf

The most complete experimental work on the solubility of copper minerals in cyanide solution was performed by Leaver and Woolf (12). The following table is compiled from their results.

[illegible]

(a) [illegible]

All [illegible] [illegible] [illegible] [illegible] [illegible] partly [illegible] [illegible] is readily [illegible] [illegible] accumulating on. The [illegible] the particle [illegible] (Fig. [illegible]) [illegible] external [illegible] mineral. [illegible] soluble [illegible] (Fig. [illegible]).

[illegible] of [illegible]

It is [illegible] copper [illegible].

[illegible]

(b) [illegible]

(i) [illegible]

The [illegible] of copper [illegible] from [illegible].

Mineral	Heads % Copper	(a) % Extraction	(b) % Extraction	Mole Ratio NaCN : Cu
Azurite $2CuCO_3.Cu(OH)_2$	0.254	100	94.5	3.12:1
Malachite $CuCO_3.Cu(OH)_2$	0.244	100	90.2	3.13:1
Chalcocite Cu_2S	0.244	100	90.2	3.11:1
Metallic Copper Cu	0.267	100	90.0	2.71:1
Cuprite Cu_2O	0.234	100	85.5	2.80:1
Bornite Cu_5FeS_4	0.264	100	70.0	3.26:1
Enargite $3Cu_2S.As_2S_5$	0.213	75.1	65.8	3.52:1
Tetrahedrite $3Cu_2S.Sb_2S_3$	0.183	43.7	21.9	3.36:1
Chrysocolla $CuSiO_3.2H_2O$	0.254	15.7	11.8	3.03:1
Chalcopyrite $CuFeS_2$	0.250	8.2	5.6	3.42:1

Note: (a) Agitation Temperature 45°C, NaCN strength 0.0100%

(b) Agitation Temperature 23°C, NaCN strength 0.0099%.

Agitation was carried out for 24 hours. The extraction percentages of column (b) are more significant than that of column (a) because none of the percentages reached 100 and thus give a better comparison between the respective minerals. The small difference in cyanide strength between column (a) and column (b) is not considered significant.

(2) Christy

Experimental work by Christy (45) on the electromotive force of minerals in cyanide solution gives an indirect confirmation to some of the dissolution values obtained by Leaver and Woolf. The voltages given in the following table are taken from Christy's results. A positive value indicates a greater tendency for the mineral to dissolve than a negative value.

Mineral	$\frac{M}{1}$ KCN	$\frac{M}{10}$ KCN	$\frac{M}{100}$ KCN	$\frac{M}{1000}$ KCN
Copper Cu	+0.81	+0.62	+ 0.37	+ 0.16
Bornite Cu_5FeS_4	+0.45	+0.25	- 0.16	------
Copper-Glance Chalcocite Cu_2S	+0.29 (?)	+0.25	+ 0.05	- 0.44
Chalcopyrite $CuFeS_2$	-0.20	-0.34	- 0.44	------
Cuprite Cu_2O	-0.43	-0.55	- 0.57	------

The voltage obtained for cuprite seems to be inconsistent. Christy states "Cuprite is also apparently very little acted on, though this may be due to its high resistance rather than a lack of tendency to dissolve." Here Christy refers to the electrical resistance of the mineral.

III METHODS OF RENDERING COPPER MINERALS INACTIVE TO CYANIDE SOLUTIONS

Having studied the mechanisms of copper dissolution and the affecting factors it is now possible to propose ways that the dissolution of copper and its undesirable effects may be controlled. These methods fall under the following three headings:

A. Removal of the copper prior to cyanidation

B. Control of the copper ion in solution

C. Cyanide regeneration

A. REMOVAL OF THE COPPER PRIOR TO CYANIDATION

1. Leaching

One of the most practical methods of removing copper from an ore, when the copper content is not sufficiently high to warrant smelting, is by leaching. If the copper content is high enough to call for smelting any associated gold will be recovered as a by-product. Here the copper is not detrimental to the gold recovery. However, where the copper is not an economic mineral but is a potential cyanicide it may be removed by leaching prior to cyanidation. Liddell (68) lists the following lixiviants for dissolving copper in order of their importance; sulphuric acid, ammonia and ammonium carbonate, ferric sulphate, sulphurous acid, ferric chloride, cupric chloride, hydrochloric acid, chlorine, and nitric acid.

[illegible]

Having [illegible] and the [illegible] way that the [illegible] effects may be [illegible]. [illegible] follows:

A. [illegible]

B. [illegible]

C. [illegible]

A. [illegible]

[illegible]

One of the [illegible] from an ore, that the [illegible] high to warrant [illegible]. [illegible] copper content [illegible] the copper [illegible]. However, [illegible] but it is [illegible] prior to [illegible]. [illegible] limits [illegible] carbon; [illegible] iron, [illegible] chlorine, [illegible].

It may be necessary to roast the ore before leaching. When an acid solvent is used the solvent must be neutralized before cyanidation is started.

2. Flotation

Another means of copper removal before cyanidation is by flotation. Taggart (74) gives the two following plans which might be applicable; flotation and cyanidation of the concentrate, and flotation and cyanidation of the tails (and concentrate). The first method may be applied to an ore in which the gold is markedly concentrated in the sulphides and the concentrate could be made amendable to cyanidation by leaching or roasting. The second plan is preferable when the gold is not concentrated with the cyanicides. If appreciable gold remains with the sulphides the concentrate may also be treated, as in the first case.

While it is possible to treat cupriferous gold ores by prior removal of the copper the application of such an operation is not always economically possible or advisable.

B. CONTROL OF THE COPPER ION IN SOLUTION

Control here covers the extent and rate of copper ion formation and the disposition of the copper ion when in solution. This phase is considered under two developments, i.e., (a) chemical and (b) physical.

(1) Chemical

Yoe (60) lists the following ways by which the

concentration of an ion may be decreased:

(a) By the formation of a very slightly soluble compound

(b) By means of the common-ion effect,

(c) By the formation of a weakly ionized compound,

(d) By the formation of a complex ion,

(e) By a change in valence of the ion, i.e. oxidation or reduction.

The application of these principles, either singularily or jointly will now be considered with respect to the copper ion.

(a) Formation of a Very Slightly Soluble Compound

For the formation of a very slightly soluble copper compound, that is, a copper precipitate, the following condition must be satisfied. The solubility product of the precipitate must be exceeded to a greater extent than that of the instability constant of the complex copper cyanide ion. The instability constant for $Cu(CN)_3^{=}$ is 5×10^{-28} (59). So that the possibilities of forming copper precipitates may be considered, the following table of solubilities (69,61) has been compiled.

COMPOUND	SOLUBILITY	Ksp !	MOL CONC. OF ANION REQUIRED TO PPT. Cu
Cuprous Bromide $CuBr$	---	$4.1x10^{-8}$	----
Cuprous Chloride $CuCl$	---	$1.0x10^{-6}$	----
Cupric Iodate $Cu(IO_3)_2$	---	$1.4x10^{-7}$	----
Cuprous Iodite CuI	---	$5x10^{-12}$	$1.1x10^{11}$
Cupric Oxalate CuC_2O_4	---	$2.9x10^{-8}$	----
Cupric Sulphide CuS	---	$2.5x10^{-41}$	$5.6x10^{-19}$
Cuprous Sulphide Cu_2S	---	$2x10^{-47}$	$1x10^{-2}$
Cuprous Thiocyanate $CuCNS$	---	$1.7x10^{-11}$	$3.8x10^{11}$
Copper Carbonate $CuCO_3$	0.3gm/L	$5.8x10^{-6}$	$1.1x10^{17}$
Copper Hydroxide $Cu(OH)_2$	$6.9x10^{-5}$ gm.mol/L	$1.3x10^{-12}$	$1.7x10^{5}$
Copper Sulphate $CuSO_4$	20.7gm/100gm H_2O	----	----
Copper Nitrate $Cu(NO_3)_2$	55.6gms/100gms H_2O	----	----
Copper Chlorate $Cu(ClO_3)_2\ 4H_2O$	62.2gms/100gms H_2O	----	----
Copper Fluoride $CuF_2.2H_2O$	0.075gms/100c.c H_2O	$1.6x10^{-9}$	$6.0x10^{7}$

COMPOUND	SoLUBILITY	Ksp !	MOL CONC. OF ANION REQUIRED TO PPT. Cu
Copper Acetate $Cu(CH_3COO)_2 \cdot H_2O$	6.79gms/100gm H_2O	---	----
Copper Tartrate $CuC_4O_6H_4 \cdot 3H_2O$	0.061gm/100cc H_2O	8.4×10^{-8}	1.9×10^{15}
Copper Fumarate $C_4H_2O_4 \cdot Cu \cdot 2H_2O$	0.02gm/100cc H_2O	---	----
Copper Maleate $C_4H_2O_4 \cdot Cu \cdot H_2O$	0.12gm/100cc H_2O	---	----
Copper Potassium Citrate $CuK_4((COOCH_2)_2C(OH)COO)_2$	43.3gm/100cc H_2O	---	----
Copper Nitrose Phenyl Hydroxylamine $Cu(C_6H_5N(NO)O)_2$	1.1×10^{-5}gm/100 cc H_2O	2.2×10^{-20}	21
Copper Cinnamate $C_{18}H_{14}O_4 \cdot Cu$	0.0304gm/100cc	7.2×10^{-9}	----
Copper Anthracene-2-Sulfonate $Cu(C_{14}H_9SO_3)_2$	0.0083gm/100cc H_2O	1.1×10^{-14}	1.6×10^{4}
Copper Diazoamidobenzene $Cu(C_6H_5N= N-N C_6H_5$	less than 0.001 gm per L CH_3OH less than o.0022 gm/L of C_2H_5OH probably less than 0.001gm/L of H_2O	less than 1.7×10^{-11}	3.8×10^{11}
Copper Helianthate $(C_{14}H_{14}N_3SO_3)_2Cu \cdot 4H_2O$	0.122gms/L	---	----
Copper Nitro Prussiate $CuFe(CN)_5NO$	6.0×10^{-5}gm mol per Liter	3.6×10^{-9}	----

! The Ksp's are for a range of temperature 15° to 35°C. There is not a significant variation of Ksp for this range of temperature.

Where only the solubility was given, the Ksp was calculated. For high solubilities the Ksp has no significance.

The molar concentration of anion required to precipitate copper from solution was calculated for a solution containing 0.100% NaCN and 0.036% copper. See Appendix (A) for sample calculations.

A perusal of the above table reveals few precipitates that could be practically formed in a cyanide solution when "free" cyanide is available. Addition of the sulphide ion presents the only possibility for the formation of a stable inorganic salt. However, in a cyanide solution which normally has a pH from 10 to 12 the sulphide ion is oxidized to the sulphate, sulphite, or thiosulphate ion. Success in the use of the sulphite ion as a precipitant of copper in an acid solution has been reported (12). For the organic compounds a salt of nitrosophenyl hydroxylamine appears to have the most promising possibility. However, the above table is far from complete and it is not hard to conceive of a salt, particularly an organic salt, that might be utilized as a copper precipitant in cyanide solutions.

(b) Addition of a Common Ion

It has been shown for a solution of 0.100 NaCN and 0.036% Cu, the Cu^+ ion concentration is $4.5x10^{-23}$ (Appendix (A)). To prevent the copper mineral dissolution, the concentration of the added common ion must be of such a value that the resulting Cu^+ ion

concentration be less than 4.5×10^{-23} gram mol per litre. This common ion concentration value may be obtained from the preceding table uner the column "Mol concentration of anion required to precipitate copper" where the copper compound is the source of copper. Thus the same considerations for copper precipitation apply here.

(c) Formation of Weakly Ionized Compounds

A review of text-books and tables fail to reveal any soluble copper compounds that are so weakly ionized that the copper ion concentration would be below the value required for the formation of the complex copper cyanide ion.

(d) Formation of a Complex Ion (other than the cyanide complex)

The requirement here would be a complex ion more stable than the copper cyanide complex. This may be obtained either with a complex having a lower value for its K instab or by a high concentration of the non-metal radical. The following table has been compiled (55) showing the complex ion, its instability constant and the necessary concentration of the non-metal radical to form the complex rather than the cyanide complex ion.

COMPLEX ION	K instab.	REQUIRED CON/ CENTRATION TO FORM THE COMPLEX
$CuCl_2^-$	2.9×10^{-6}	$1.9 \times 10^{+7}$
$CuBr_2^-$	1.2×10^{-6}	$1.2 \times 10^{+7}$

COMPLEX ION	K instab.	REQUIRED CONCENTRATION TO FORM THE COMPLEX
CuI_2	$1.4x10^{-9}$	$4.2x10^{5}$
$Cu(NH_3)_2^{+}$	$1.35x10^{-11}$	$4.1x10^{4}$
$Cu(NH_3)_4^{++}$	$4.56x10^{-14}$	87
Cupritartrate $Cu(OHCCOO)_2^{=}$	---	---
Substituted Ammonia Complexes e.g. $Cu(C_2H_5.NH_2)_4^{++}$	---	---

(See Appendix (A) for sample computation)

The above table shows that there are few copper complexes that are more stable than the cyanide complex. The substituted ammonia complexes are probably more stable than the ammonia complexes and may possibly be utilized for the prevention of the cyanide complex. It is noted that the ammonia complexes are cations rather than anions and might form an insoluble compound with the cyanide anions as the example below:

$$Cu(NH_4)_3^{++} + 2CN^- = Cu(NH_4)_3(CN)_2$$

(e) Change in Valence of the Copper Ion

The application of this principle appears to have interesting possibilities. As previously noted the mechanism whereby the cupric ion forms the complex is one of oxidation-reduction as follows:

(1) $Cu^{++} + 2CN^- = Cu(CN)_2$

(2) $2Cu(CN)_2 = 2CuCN/ + C_2N_2$ -reduction of Cu^{++} to Cu^{+}

(3) $CuCN + 2CN^{-} = Cu(CN)_3^{=}$

$2Cu^{++} + 2e = 2Cu^{+}$

$2CN^{-} = C_2N_2 + 2e$

(4) $Cu^{++} + 3CN^{-} + e = Cu(CN)_3^{=}$ -overall reaction

The degree of reversibility of this reaction can be gauged by its oxidation potential. It may be calculated as follows:

(1) $Cu + 3CN^{-} = Cu(CN)_3^{=} + e$ $E^{o} = +1.09$ (26)

(2) $Cu^{++} + 2e = Cu$ $E^{o} = +0.33$ (58)

(1) + (2) $Cu^{++} + 3CN^{-} + e = Cu(CN)_3^{=}$ $E^{o} = +1.42$

This means the formation of the complex is strongly favored and it is necessary for an oxidizer to have an oxidation potential of $E^{o} = -1.42$ to oxidize the $Cu(CN)_3^{=}$ to Cu^{++}. Consider the case of chlorine as an oxidizing agent.

(a) $\frac{1}{2}Cl_2 + e = Cl^{-}$ $E^{o} = +1.36$

(b) $Cu(CN)_3^{=} = Cu^{++} + 3CN^{-} + e$

(a) + (b)

$Cu(CN)_3^{=} + \frac{1}{2}Cl_2 = Cu^{++} + 3CN^{-} + Cl^{-}$ $E^{o} = E^{o}_{Cu} + E^{o}_{Cl}$

$= -1.43 + 1.36$

$= -0.06$

Thus the reaction is not spontaneous at unit activity, and the $Cu(CN)_3^{=}$ is not oxidized.

However, this applies only at unit activity and it is possible to make the reaction spontaneous by varying the concentrations of the reactants. The relationship of concentrations to the oxidation potential is shown as

follows:

$$E_T = E_T^o - .059 \log \frac{C_{Cu^{++}} \times C_{CN^-} \times C_{Cl^-}}{C_{CuCN_3^{=}} \times C_{\frac{1}{2}Cl}} \qquad (73)$$

$$= -0.06 - .059 \log \frac{C_{Cu^{++}} \times C_{CN^-} \times C_{Cl^-}}{C_{CuCN_3^{=}} \times C_{\frac{1}{2}Cl_2}}$$

With a low concentration of Cu^{++}, CN^-, and Cl^-, and a high concentration of $CuCN_3^{=}$ and Cl_2 it is possible to reverse the reaction.

Additional to the foregoing chemical methods for control of the copper ion in solution are those arising from the direct factors affecting the copper dissolution. These are as follows:

(f) pH. It is evident that a low pH favors a limited dissociation of HCN resulting in low copper dissolution.

(g) Oxygen. By maintaining low oxygen content of the solution the amount of copper going into solution is reduced.

(h) Cyanide Strength. The copper solubility is directly proportionate to the cyanide strength of the solution.

(i) Temperature. Low temperature favors low copper dissolution.

(j) Electrochemical. Addition of minerals or

salts electronegative to the copper minerals may control the dissolution.

(k) Catalytic Action. It is conceivalbe that a negative catalyst might be found which hinders the copper dissolution.

(l) Selective Adsorption. Closely akin to catalysis is selective adsorption. The copper ion may be adsorped onto a surface in preference to the formation of the cyanide complex.

(m) Coating of Mineral Surfaces. By coating the copper mineral surfaces by a substance that is impervious to the cyanide solution, the copper dissolution may be limited. The means, by which the mineral surface is coated, may be physical or chemical.

(2) Physical

(a) Time of Contact. By limiting the time of contact of the ore with the cyanide solution the copper dissolution may be kept to a minimum.

(b) Size of Grain. A course grind of the copper minerals would make for less copper dissolution than a fine grind would.

C. CYANIDE REGENERATION

The principle of cyanide regeneration is now considered with particular application to the copper minerals. In the usual precipitation of gold with zinc dust only a part of the copper appears to precipitate,

because in cyanide solutions the copper is only slightly more "noble" than the precipitating zinc.

Thus, much of the copper as the cyanide complex ion is found in the barren solution. It is from this barren solution that attempts are made to free the cyanide from the copper. The following regeneration possibilities are discussed:

(1) Electrolysis
(2) Precipitation methods
(3) Distillation

(1) Electrolysis. Fundamentally the regeneration of cyanide by electrolysis is simple. Electrodes are placed in a cyanide bath and a voltage applied sufficient to break down the copper cyanide complex ion. Cyanide is regenerated at the cathode. Practically, the process is complex requiring close control of voltage and current density, otherwise there is appreciable destruction of cyanide. Halferdahl (22) states,"Electrolysis of original-ore cyanide solutions has not been successful in precipitating the copper and regenerating the cyanide."

(2) Precipitation methods. As stated when gold is precipitated by zinc only part of the copper is precipitated. However, prolonged treatment of the barren solution with zinc will precipitate all the copper but

the cyanide is merely transferred from the copper complex ion to the zinc complex and necessitates cyanide regeneration from the zinc complex. The most practical approach to regeneration has been by acidifying the solution and taking the copper out of solution as a sulphide by the addition of sodium sulphide (12), or by treatment with sulphur dioxide (23). The cyanide is recovered as HCN gas which is adsorbed in an alkaline solution.

(3) Distillation. This process, as yet, has been limited to laboratory practice for the determination of total cyanide (11). The method comprises acidifying the solution with hydrochloric acid and distilling into an alkaline solution. The distillate is HCN. It would appear to be a costly process and not commercially applicable.

As in the case of copper removal prior to cyanidation, cyanide regeneration presents a solution that may not be economically possible or advisable.

OUTLINE

of

POSSIBLE INVESTIGATIONS

OUTLINE OF POSSIBLE INVESTIGATIONS

Table of Contents

I Chemical

- A. Oxygen and Cyanide Concentration
- B. pH and Oxidizers
- C. Temperature
- D. Precipitation
- E. Mineral Coating
- F. Catalysis

II Electrochemical

III Physical

- A. Degree of Grind
- B. Time of Contact

OUTLINE OF POSSIBLE INVESTIGATIONS

The study of cyanidation and the chemistry of copper in cyanide solutions indicate three main approaches to the problem of limiting the detrimental effects of copper in the cyanidation of cupriferous gold ore. These are: first, the elimination of copper prior to cyanidation; second, the control of copper dissolution in cyanidation; and finally, the removal of the undesirable effects after gold dissolution, namely, cyanide regeneration. Application of the first and third approach have proven to be a costly remedy. At this time, the second approach offers the most economic promise, in that the solving of this problem lies in the addition of small amounts of reagents and the correct control of operating conditions. For this reason, discussion will be restricted to this approach.

Past work on the dissolution of both gold and copper under varying circumstances indicate the existence of a differential between the dissolution rates. The exploitation of this differential appears to offer the best possibilities of a solution to this difficulty of controlling copper dissolution and effecting a favorable gold recovery. A study of parallel dissolution changes, under similar variable conditions, is necessary to determine if a differential exists between the two dissolution rates.

The significance of the dissolution differential is illustrated in the following manner. If a common factor decreases the solubility of copper to a greater extent than the gold dissolution, it may be preferable to operate at a decreased copper solubility. The lowered gold dissolution may be compensated by a longer period of agitation to obtain the same over-all gold recovery. Further, if a common factor increases the solubility of gold to a greater extent than the copper dissolution, it may be advisable to operate at the increased gold solubility with a shorter period of agitation to compensate the increased copper solubility rate. The ideal differential would be one where the copper solubility is nil and the gold dissolution reaches a maximum.

Study of factors (that may be classed as chemical, electrochemical, and physical) affecting the dissolution of gold and copper should reveal the potentialities of a differential rate where it exists.

I CHEMICAL

A. OXYGEN CONTENT AND CYANIDE STRENGTH

The reaction for the dissolution of gold and copper has been suggested to be a heterogeneous reaction in which both oxygen and cyanide concentrations are interdependent in the mineral dissolution. If this is so,

there is no reason to suspect a differential existing when either reactant is varied. However, if the dissolution mechanisms for both copper and gold differ because gold is in the native state and copper usually is found as a compound, then there may be different rates of dissolution for each mineral.

Unfortunately no experimental values are obtainable for copper solubility when both cyanide and oxygen concentrations were varied proportionately, or when the cyanide strength was kept constant and the oxygen concentration varied. In investigations where the cyanide strength was varied and the oxygen concentration remained constant the following results were observed:

(1) The copper content increased proportionately with increase of cyanide strength, that is, with the cyanide strength doubled, the copper solubility increased two fold.

(2) The gold solubility increased rapidly from 0.010% NaCN to 0.025% NaCN. By doubling the cyanide concentration, the gold solubility was raised to six times its first value. Maximum dissolution was obtained at 0.050% NaCN but the increased gold solubility at 0.050% NaCN was only 1.3 times that at 0.025% NaCN. After a strength of 0.050% NaCN the gold dissolution fell off.

Thus it would appear that a very favorable differential exists up to 0.025% NaCN. After this point has passed the differential decreases and finally becomes negative.

B. pH AND OXIDIZERS

From the inter-relation of pH and HCN dissociation it is evident that pH controls the "effective" strength of the cyanide concentration. Therefore considerations that apply to cyanide strength apply to pH. But change of pH has additional effects in cyanide solutions such as the repressing of thiocyanate formation when a high hydrogen ion concentration is maintained. So it is possible that pH control has other influences in setting up a differential dissolution rate.

When an oxidizer primarily supplies oxygen to the cyanide solution the effect is as previously noted. But oxidizers do not necessarily supply oxygen and, if this is the case, their influences on gold and copper differ. The following fundamental reactions are examined:

(1) $Au + 2CN^- = Au(CN)_2^= + e$,

(2) $Cu + 3CN^- = Cu(CN)_3^= + e$,

(3) $Cu^{++} + 3CN^- + e = Cu(CN)_3^=$.

Equations (2) and (3) may be combined:

$$Cu + 3CN^- = Cu^{++} + 3CN^- + 2e$$

This means that if a strong oxidizing agent was used the cyanide consuming complex might be eliminated. The gold could be oxidized to the trivalent form but this would

not be undesirable. The overall effect would be the same as maintaining a favorable differential.

C. TEMPERATURE

No significant differential appears to exist with variation of temperature. Mellor (50) gives the following values for the dissolution of Au and Cu at different temperatures:

Metal	Milligrams dissolved per Sq.Cm. of Surface		Ratio (2)/(1)
	(1) 15.6°	(2) 71°	
Copper	0.053	1.263	24
Gold	0.009	0.229	25

D. PRECIPITATION

Premature precipitation of gold is not wanted. The possibility of precipitating copper from alkaline cyanide solution has been discussed. Any method of precipitating copper without affecting gold dissolution would promote a desirable differential.

E. MINERAL COATING

The term mineral coating is used here in its broadest sense. It includes all types of adsorption and the surface coating of a mineral by non polar compounds. Any substance which coats copper in preference to gold would tend to establish a favorable differential.

F. CATALYSIS

To maintain a favorable differential dissolution rate the catalyst must accelerate the gold dissolution to a greater extent than the copper dissolution. In the case of a negative catalyst the copper solubility must be retarded to a greater degree than the gold dissolution.

II ELECTROCHEMICAL

Application of electrochemical principles offers interesting possibilities in establishing a differential between the dissolution rates of copper and gold. The table of electromotive forces for metals and minerals prepared by Christy (45) for a cyanide solution of 0.065% strength is re-examined at this time.

	E Volts
Al	+ 0.76
Zn	+ 0.59
Cu	+ 0.37
Au	+ 0.09
Chalcocite	+ 0.05
Pb	+ 0.01
Sb	- 0.03
Ag	- 0.05
Bornite	- 0.16
As	- 0.21
Iron	- 0.24
Niccolite	- 0.44
Pyrite	- 0.48
Stephanite	- 0.52 (?)
Arsenopyrite	- 0.54
Argentite	- 0.55
Galena	- 0.56
Stibnite	- 0.56
Cuprite	- 0.57 (?)

As stated in the chapter on cyanidation, minerals below gold, in the series, accelerate the dissolution of gold while minerals above deter the gold dissolution. Similarily the copper solubility may be aided or retarded by the presence of other minerals. The table shows that the majority of the copper minerals are below gold in the series. So if a mineral which is above the copper minerals but below gold was employed, the gold dissolution would be promoted and the copper solubility retarded. Consider this example of a cyanide solution containing gold, lead and copper compounds. The copper compounds aid the lead and gold dissolution. The lead aids the gold dissolution but what is more important, the lead retards the copper dissolution. The gold tends to discourage copper solubility but is not, normally, in sufficient quantities to be effective. Thus it is shown how application of electrochemical principles may be of help in eliminating the copper minerals from the class of cyanicides.

III PHYSICAL

A. DEGREE OF GRIND

As the grain size of the copper minerals is a factor in the copper mineral dissolution, it is evident that over-grinding should be avoided and grinding should be carried out only to the extent of releasing the gold

to the solvent action of the cyanide solution.

B. TIME OF CONTACT OR AGITATION

This factor cannot establish a differential but can be used to take advantage of any existent differential.

EXPERIMENTAL WORK

EXPERIMENTAL WORK

Table of Contents

I. Laboratory Procedure

- A. Detailed Description of Cyanidation Charge
  1. Ore Charge
  2. Solution
  3. Additional Reagents
- B. Details of a Test
- C. Methods of Analysis and Recording of Data
  1. Cyanide
  2. Alkalinity
  3. Copper
  4. Gold
  5. Additional Determinations

II. Investigations

Investigations Numbers

1. Agitation time for Cyanidation Tests
2. Effect of Alkalinity (Lime) on Copper Solubility
3. Effect of Alkalinity (Sodium Hydroxide) on Copper Solubility
4. Effect of Cyanide Strength on Copper Solubility
5. Effect of Copper Solubility on Alkalinity
6. Effect of Cyanide Strength and Time on Copper Solubility
7. Effect of Amines on Copper Solubility
8. Effect of an Amine on Gold Extraction and Copper Solubility
9. Effect of Xanthates and Stearic Acid on Copper Solubility

10. Effect of pH on Copper Solubility Using Phosphates as a Buffer Reagent

11. Effect of pH on Copper Solubility Using Various Buffer Reagents

12. Effect of pH on Gold Extraction

13. Effect of Aluminum Oxide on Copper Solubility

14. Effect of Litharge on Copper Solubility in a Lime Circuit

15. Effect of Lead Acetate on Copper Solubility in a Lime Circuit

16. Effect of Lead Silicate on Copper Solubility in a Lime Circuit

17. Effect of Litharge on Gold Extraction and Copper Solubility in a Lime Circuit

18. Effect of Litharge on Copper Solubility in a Sodium Hydroxide Circuit

19. Effect of Litharge on a Gold Extraction and Copper Solubility in a Sodium Hydroxide Circuit

20. Effect of Litharge on Gold Extraction and Copper Solubility in a Lime Circuit Sodium Hydroxide Circuit, and in a Circuit in which no Alkali was Added.

21. Effect of Sodium Hydroxide and Litharge on Gold Extraction and Copper Solubility

22. Effect of Cyanide Strength and Litharge on Gold Extraction and Copper Solubility

23. Effect of pH and Litharge on Copper Solubility

24. Effect of a Strong Oxidizer on Copper Solubility

25. Effect of Sodium Peroxide and Litharge on Copper Solubility

26. Effect of Sodium Peroxide and Litharge on Copper Solubility

27. Effect of Litharge and Sodium Peroxide on Gold Extraction and Copper Solubility

28. Effect of Phosphate, Litharge and Sodium Peroxide on Gold Extraction and Copper Solubility

29. Effect of Litharge and Sodium Peroxide on Gold Extraction and Copper Solubility for a Prolonged Period of Agitation

30. Effect of Litharge on Gold Extraction and Copper Solubility in Ores of Different Copper Content

EXPERIMENTAL WORK

I LABORATORY PROCEDURE

Cyanidation tests were carried out by agitating ore, cyanide solution and additional reagents for a period of time. At the completion of agitation the solutions were separated from the solids by filtering and stored for subsequent analysis.

A. DETAILED DESCRIPTION OF A CYANIDATION CHARGE

(1) Ore Charge

Investigations required two types of ore charges as the work was carried out in a two stage manner, comprising first, preliminary tests in which factors affecting the solubility of copper were explored and, second, in which the effects of these factors on gold dissolution were examined.

In the first case the ore charge for cyanidation consisted of 5 grams of copper concentrate and 195 grams of Ottawa sand and was designated a Copper Sulphide Ore. In the second case it consisted of 100 grams of gold pyrite concentrate, 5 grams of copper concentrate and 95 grams of Ottawa sand and was designated a Pyrite Copper Sulphide Ore. A variation of the second charge was made by deleting the copper concentrate, the charge being designated a Pyrite Ore.

A pyrite concentrate was used to supply the gold in the cyanidation tests. It was composed of 86% pyrite, silicious gangue and assayed two ounces of gold per ton of ore. The fineness of grind is shown in Table A.

Copper concentrate was used to provide soluble copper in the cyanidation charge. The minerals as determined from polished sections by a mineral count, described in Appendix B, were: Chalcopyrite 26.9%, bornite 26.1%, pyrite 12.4%, covellite 0.8%, Chalcocite 0.6% and gangue 33.2%. The copper concentrate assayed 26.8% copper, 16.3% iron, 4.110 ounces of silver per ton ore and 0.120 ounces of gold per ton ore. Fineness of grind is shown in Table A.

Ottawa sand was used as a filler to make up the 200 grams of ore when varying amounts of copper concentrate or pyrite base or both were used. Fineness of grind is shown in Table A.

Table A Screen Analysis of the Different Ore Products used in Making up the Composite Ore Charge

MESH	PYRITE CONC.	COPPER CONC.	OTTAWA SD.
-20 + 28	----	----	100.0
-28 + 35	0.2	----	----
-35 + 48	0.7	----	----
-48 + 65	4.7	----	----
-65 + 100	18.1	----	----
-100 + 150	21.8	2.2	----
-150 + 200	13.7	7.6	----
-200	40.8	90.2	----
	100.0	100.0	100.0

(2) Solution

The cyanidation tests were carried out in 1000 milliliters of 0.100% cyanide solution. The 0.100% cyanide strength was employed to provide a reserve in cyanide over the theoretical optimum of 0.05% cyanide, should the cyanide consumption become excessive.

The high liquid to solid ratio was adopted so that the cyanide and alkali concentration would not change too much from start to completion of agitation, without further additions during the test.

(3) Additional Reagents

Protective alkali was supplied by adding 0.300 grams of lime, with 83.5% available CaO to give a 0.025% CaO solution. Where other alkali was used on equivalent amount was added.

Further addition reagents, when employed, were

added as reported for the individual tests.

B. DETAILS OF A TEST

Cyanidation tests were carried out in two quart sealers and, when charged with 200 grams of ore and 1000 milliliters of cyanide solution, were a little more than half full. In making up a cyanidation charge the ore, lime and additional reagents were weighed into the sealers. The cyanide solution was prepared by placing 20 cc. of 5% sodium cyanide solution into 1000 milliliter measuring flask. This was made up to the mark with tap water and immediately prior to the beginning of a cyanidation test the cyanide solution was added to the sealer. The jars were then sealed, placed in the agitator and time recorded at the beginning of agitation. The jars were agitated by tumbling and over end in a rack rotated at 28 r.p.m. At the completion of the test the solution was separated from the ore by pressure filtering and stored in stoppered flasks for subsequent analysis.

C. METHODS OF ANALYSIS AND RECORDING OF DATA

(1) Cyanide

The cyanide strength was determined by titrating the solution with a 0.217% $AgNO_3$ solution. On a 25 cc. sample 1cc of $AgNO_3$ is equivalent to 0.005% NaCN. The cyanide range was reported in per cent solution of sodium cyanide at the beginning and end of agitation

and the consumption in pounds of sodium cyanide per ton of ore.

(2) Alkalinity

The alkalinity was determined by titrating the solution with a 0.219% H_2SO_4 solution. On a 25 cc. sample, 1cc. of H_2SO_4 is equivalent to 0.005% CaO. The alkalinity range was reported in per cent CaO and the consumption in pounds of CaO per ton of ore. Where other alkali was used the alkalinity was reported in CaO equivalents.

(3) Copper

Copper in solution was determined colorimetrically and reported as per cent in solution. The relation between per cent cyanide consumption and per cent copper in solution was reported as "Molecular Ratio." This calculation was included in the tables were applicable and was determined by dividing the sodium cyanide consumption in mols. by the copper in solution in mols.

(4) Gold

The gold extraction was determined by assaying of the cyanide solution only, (Lead boat method) rather than by an assay of heads and tails. This procedure was adopted for two reasons, first, because any variation in gold content in the heads would be reduced, and therefore minimize the screening effect these might have on variations caused by other factors, and second,

it meant fewer determinations were required to obtain the required data. This procedure necessitated referring all results of tests to a standard test and was accomplished by use of the term "Relative Gold Extraction Percent." It was calculated as follows: in each series of tests one standard run (cyanidation of 100 grams of the gold pyrite concentrate and 100 gms. of Ottawa sand in a lime cyanide solution) was made. The gold extracted for the standard was considered as 100% relative gold extraction and the remaining tests proportionately so. Further, that a comparison of the different gold and cyanide consumption might be made, an arbitrary ratio of gold extraction percent over cyanide consumption in pounds per ton of ore was established. This ratio was included in the tables where applicable.

(5) Additional Determinations

Reducing power was determined for several of the tests and recorded as the number of cc. of $\frac{N}{10}$ $KMnO_4$ per liter of solution.

The pH of solutions was determined by the Coleman pH Electrometer. When applicable corrections for Na^+ were applied as given by Dole (75).

II INVESTIGATIONS

INVESTIGATION No. 1 Tests to determine the time of cyanidation which would give sufficient recovery for subsequent experimental work - Table 1.

Standard tests were run on 100 grams of pyrite concentrate and 100 grams of Ottawa Sand for varying agitation times. The results indicated that a two hour agitation period would be sufficient to give trends and variations under other conditions. Moreover, the short agitation time would facilitate the running of more tests.

Table 1. - Tests to determine the Time of Cyanidation which would give Sufficient Recovery for Subsequent Experimental Work.

Test No.	Agitation Time	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	Gold Heads Oz./ton Ore	Gold Tails Oz./ton Ore	Recovery %
13	1:30	.100-.0740	2.60	.025-.0145	1.05	.920	.600	34.8
16	2:00	.100-.0795	2.05	.025-.0100	1.50	.920	.220	76.1
18	2:30	.100-.0775	2.25	.025-.0125	1.25	.920	.200	78.3
19	3:00	.100-.0800	2.00	.025-.0110	1.40	.920	.200	78.3
21	2:00	.100-.0875	1.25	.025-.0125	1.25	.920	.245	73.3
22	2:00	.100-.0825	1.75	.025-.0130	1.20	.920	.240	73.9

INVESTIGATION No. 2 Effect of varying lime alkalinity on the solubility of copper in the cyanidation of a copper sulphide ore - Table 2

Tests were performed on a copper sulphide ore in which the CaO content was varied from 0.00 to 0.675%.

Results:

Cu - Solubility constant at .034%,

NaCN - Consumption increased gradually from 7.45 lb. to 8.10 lb. per ton ore,

NaCN/Cu - Constant at 3.0,

CaO - Consumption increased. However, beyond .075% the solubility of CaO was exceeded and thus lime consumption was not recorded.

Discussion of Results:

The increased cyanide consumption with increase in CaO is probably due to the oxidation of the CN^- ion, by the increased OH^- concentration, in accordance with the equation:

$$CN^- + 2OH^- = CNO^- + H_2O + 2(-) \qquad dF = -44,190$$

The free energy change favors the reaction moving to the right. Although ordinarily the OH^- concentration is small, with excessive CaO addition this concentration may become sufficient to give a determinable cyanide consumption.

Table 2. - Effect of Varying Lime Alkalinity (CaO) on the Solubility of Copper in the Cyanidation of a Copper Sulfide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
83	.100-.0255	7.45	.000-.009	-0.90	.034	2.3
84	.100-.0250	7.50	.025-.020	0.50	.034	2.9
85	.100-.0250	7.50	.050-.043	0.70	.034	2.9
86	.100-.0240	7.60	.075-.067	0.80	.036	2.7
87	.100-.0230	7.70	.150-.115	---	.038	2.6
88	.100-.0225	7.75	.225-.121	---	.036	2.3
89	.100-.0220	7.80	.300-.130	---	.034	3.0
90	.100-.0210	7.90	.375-.134	---	.034	3.0
91	.100-.0205	7.95	.450-.129	---	.032	3.2
92	.100-.0220	8.00	.525-.124	---	.032	3.2
93	.100-.0195	8.05	.600-.117	---	.032	3.3
94	.100-.0190	8.10	.675-.112	---	.032	3.3

In tests 87 to 94, the CaO added was in excess of its solubility and thus lime consumption was not given for these tests.

INVESTIGATION No. 3   Effect of varying sodium hydroxide alkalinity on the solubility of copper in the cyanidation of a copper sulphide ore - Table 3.

Tests were run on a copper sulphide ore, varying the NaOH content from 0.025 to 0.600% NaOH.

Results:

Cu - Solubility constant,

NaCN - A gradual increase in consumption from
    6.95 to 8.00 lb/ton ore,

NaCN/Cu - Constant at 3.0,

NaOH - Consumption increased from 0.15 to 3.20
    lb. per ton ore.

Discussion of Results:

The increased cyanide and sodium hydroxide consumption may be attributed to the oxidation of the cyanide ion to the cyanate ion by OH^-, as detailed in Investigation No. 2.

Table 3. - Effect of Varying Sodium Hydroxide Alkalinity (NaOH) on the Solubility of Copper in the Cyanidation of a Copper Sulfide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	NaOH = CaO Range % Soln.	NaOH = CaO Consump. lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN / Cu
223	.100-.0305	6.95	.025-.0235	0.15	.030	3.0
224	.100-.0305	6.95	.050-.0525	-0.25	.030	3.0
225	.100-.0305	6.95	.075-.0745	0.05	.030	3.0
226	.100-.0310	6.90	.100-.0985	0.15	.030	3.0
227	.100-.0290	7.10	.200-.1850	1.50	.032	2.9
228	.100-.0210	7.90	.400-.3775	2.25	.032	3.2
229	.100-.0200	8.00	.600-.5680	3.20	.034	3.1

INVESTIGATION NO. 4. Effect of varying sodium cyanide strength on the solubility of copper and cyanide consumption in the cyanidation of a copper sulphide ore - Table 4 - Fig. 1.

Tests were carried out on a copper sulphide ore in which the cyanide strength was increased from 0.00 to 0.500% sodium cyanide.

Results:

Cu - Solubility increased directly proportional to the cyanide concentration up to a 0.100% cyanide solution. From 0.100 to 0.500% solution the increase in copper solubility dropped off,

NaCN - Consumption increased comparable to the increase in copper solubility,

NaCN/Cu - Constant ratio maintained,

CaO - Increased consumption with increase in cyanide concentration.

Discussion of Results:

The curve for copper solubility with increasing cyanide concentration (Fig. 1) gives a curve with two definite slopes. A detailed study of these slopes and possible influencing factors, however, fails to reveal any logical explanation.

The gradual decrease in lime consumption with increased copper solubility, until an actual increase

in percent alkalinity is noted at the end of agitation (negative consumption) may be explained by the equation for the dissolution of copper:

$4Cu + 12NaCN + O_2 + 2H_2O = 4Na_2Cu(CN)_3 + 4NaOH$

For each molecule of copper dissolved one molecule of sodium hydroxide is formed which would account for the increased alkalinity. To provide further confirmatory evidence of an actual formation of NaOH (increased alkalinity) occurring with copper dissolution, Investigation No. 5 was carried out.

Table 4. - Effect of Varying Sodium Cyanide (NaCN) strength on the Solubility of Copper and Cyanide Consumption in the Cyanidation of a Copper Sulfide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
95	Nil	Nil	.025-.0140	1.10	Nil	---
96	.025-.003	2.2	.025-.0160	0.90	.010	2.9
97	.050-.008	4.2	.025-.0170	0.80	.020	2.7
98	.075-.013	6.2	.025-.0200	0.50	.030	2.7
99	.100-.021	7.9	.025-.0190	0.60	.040	2.6
100	.200-.076	12.4	.025-.0210	0.40	.054	3.0
101	.300-.151	14.9	.025-.0260	-0.10	.066	2.9
102	.400-.228	17.2	.025-.0320	-0.70	.078	2.9
103	.500-.310	19.0	.025-.0355	-1.05	.088	2.8

INVESTIGATION No. 5. Tests to show the effect of copper solubility on alkalinity - Table 5.

Tests 206-209 were carried out on a copper sulphide ore and tests 210-213 on Ottawa sand.

Discussion of Results:

The equation for dissolution of copper is as follows:

$$4Cu + 12NaCN + O_2 + 2H_2O = 4Na_2Cu(CN)_3 + 4NaOH$$

254 160

From the equation the following equivalents exist:

$$1 \text{ gm. } Cu \equiv 0.63 \text{ gms. } NaOH$$

$$\text{Thus } .034\% \; Cu \equiv .021\% \; NaOH \equiv .014\% \; CaO$$

From Table 5 we have:

Test No.		CaO equiv.%
212	Sand + NaCN	.0030
208	Sand + NaCN + Cu + Cu reaction	.0110
	(1) 208-212, i.e. Cu + Cu reaction	.0080
206	Sand + Cu	.0005
210	Sand	.0020
	(2) 206-210, i.e. Cu	-.0015

CaO equivalent attributed to Cu reaction equals (1) - (2)
.0080 + .0015 = .0095%

With the addition of CaO (tests 207, 209, 211 and 213) and calculating as above, .0075% equivalent CaO is formed as a result of copper dissolution.

Thus, from theoretical considerations the dissolution of .034% copper produces an equivalent alkalinity of .014% CaO, whereas, from actual test work .034%

copper produces an equivalent alkalinity of .0095% CaO. The results appear sufficiently close to support the hypothesis of OH^- formation with copper dissolution, particularly as the tests are more of a qualitative than quantitative nature.

Table 5. - Tests to Show the Effect of Copper Solubility on Alkalinity

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
206	Nil	Nil	.000-.0005	-0.05	Nil	---
207	Nil	Nil	.025-.0210	+0.40	Nil	---
208	.100-.029	7.10	.000-.0110	-1.10	.034	2.7
209	.100-.026	7.40	.025-.0280	-0.30	.034	2.8
210	Nil	Nil	.000-.0020	-0.20	---	---
211	Nil	Nil	.025-.0225	+0.25	---	---
212	.100-.098	0.20	.000-.0030	-0.30	---	---
213	.100-.098	0.20	.025-.0220	+0.30	---	---

Tests 206-209 run on a copper sulphide ore
Tests 210-213 run on Ottawa sand.

INVESTIGATION No. 6 Effect of varying sodium cyanide strength and time on the solubility of copper in the cyanidation of a copper sulphide ore - Table 6-Figs.2&3.

Tests were run on a copper sulphide ore with cyanide strengths of .025, .050 and .100 per cent, for a period of ten hours agitation. Solutions were titrated after each hour for the first six hours and original cyanide strength restored.

Results:

Cu - Solubility increased proportionately for both time and cyanidestrength. For example: 6:00 hours agitation with .050% cyanide gave a copper solutility of .044%; 3:00 hrs. agitation with .100% cyanide gave a copper solubility of .044%,

NaCN - Consumption corresponded to copper solubility,

NaCN/Cu - Constant ratio at 3,

CaO - Consumption decreased with increasing cyanide strength,

R.P. - Reducing power increased with increased cyanide strength and corresponding copper solubility.

Discussion of Results:

To illustrate the relationship of copper solubility with time and cyanide strength the following table was

compiled from Table 6.

Agitation Time Hours	Cyanide Strength Per Cent	Cu Sol'y. Per Cent
4	0.025	.026
2	0.050	.022
6	0.025	.030
3	0.050	.028
4	0.050	.036
2	0.100	.034
6	0.050	.044
3	0.100	.044
10	0.050	.060
5	0.100	.064

To further indicate the direct proportionality between time and cyanide strength, Fig. 3 was constructed by plotting the product of time and cyanide strength against the per cent copper in solution. This resulted in an almost straight line curve with a gradual dropping off at higher per cent NaCN x time, because of the gradual depletion of the available copper content. The close proximity of points with the same per cent NaCN x time product (arrived at from different strengths and time) and their respective copper solubilities, further illustrates the direct interdependence of time and strength on copper solubility.

Table 6. - Effect of Varying Sodium Cyanide Strength and Time on the Solubility of Copper in the Cyanidation of a Copper Sulphide Ore

Test No.	Time Accumul.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	R.P.	Copper in Soln. %	Mol. Ratio NaCN/Cu
306	1:00	.025-.0035	2.15				-	
	2:00	.025-.0130	1.20				.012	3.6
	3:00	.025-.0155	0.95				.020	2.8
	4:00	.025-.0170	0.80				.026	2.6
	5:00	.025-.0145	1.05				.026	3.1
	6:00	.025-.0185	.65				.030	2.95
	6:15	.025-.0215	.35	.025-.0225	+0.15	64		
			7.15					
307	1:00	.050-.0140	3.60				-	
	2:00	.050-.0290	2.20				.022	3.4
	3:00	.050-.0360	1.40				.028	3.3
	4:00	.050-.0360	1.40				.036	3.1
	5:00	.050-.0400	1.00				.036	3.5
	6:00	.050-.0420	0.80				.044	3.1
	10:00	.050-.0305	1.95	.025-.030	-0.50	192	.060	2.7
			12.35					
308	1:00	.100-.0420	5.80				-	
	2:00	.100-.0625	3.75				.034	3.65
	3:00	.100-.0780	2.20				.044	3.5
	4:00	.100-.0875	1.25				.052	3.25
	5:00	.100-.0865	1.35				.064	2.9
	6:00	.100-.0930	0.70				.068	2.9
	10:00	.100-.0810	1.90	.025-0.32	-0.70	264	.068	3.25
			16.95					

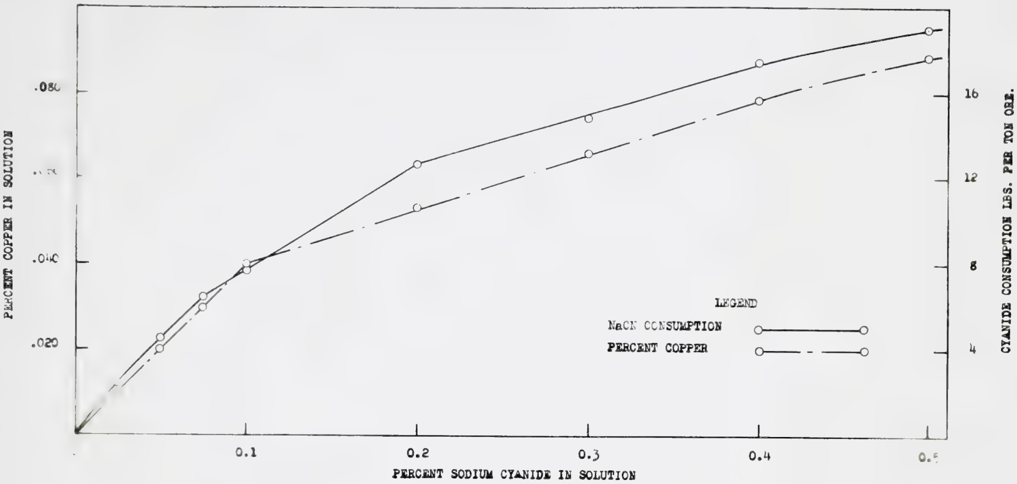

FIG. 1 EFFECT OF VARYING SODIUM CYANIDE STRENGTH ON THE SOLUBILITY OF COPPER AND SODIUM CYANIDE CONSUMPTION IN THE CYANIDATION OF A COPPER SULFIDE ORE.

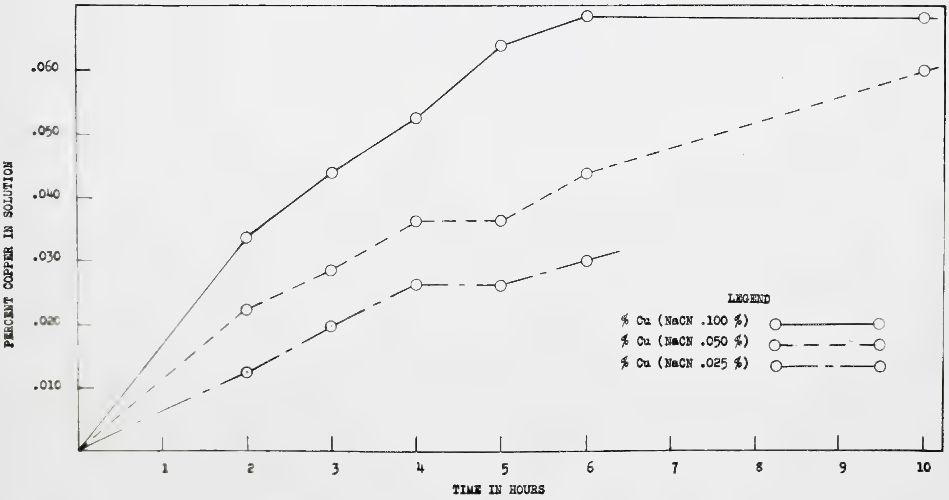

FIG. 2 EFFECT OF VARYING NaCN STRENGTHS AND TIME ON THE SOLUBILITY OF COPPER IN THE CYANIDATION OF A COPPER SULPHIDE ORE.

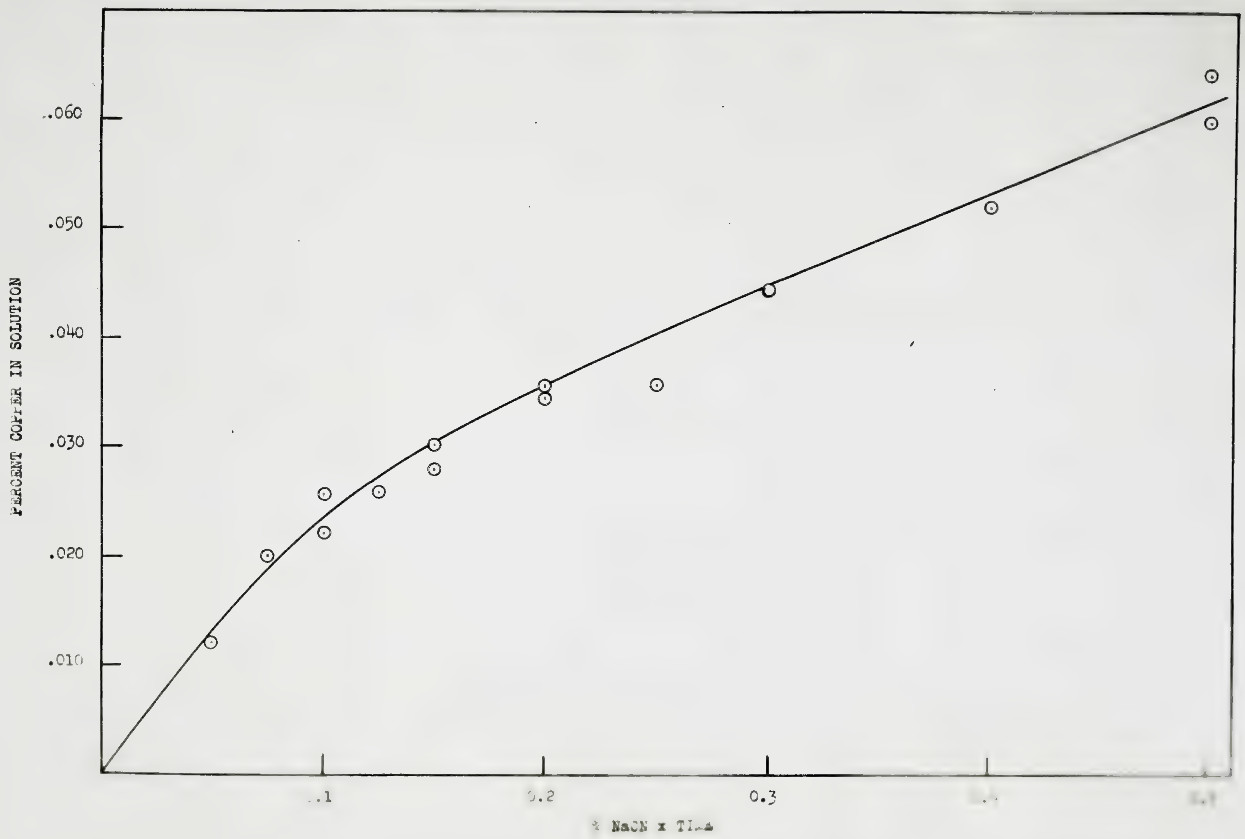

FIG. 3 RELATION BETWEEN CYANIDE STRENGTH AND TIME, AND COPPER SOLUBILITY IN WHICH THE PRODUCT OF PERCENT CYANIDE STRENGTH AND TIME IS PLOTTED AGAINST PERCENT COPPER IN SOLUTION.

INVESTIGATION No. 7. Effect of various amines on the solubility of copper in the cyanidation of a copper sulphide ore - Table 7, Fig. 4.

To study the effect of various organic salts as a possible means of controlling copper solubility by adsorption, mineral coating or precipitation, tests were run on a copper sulphide ore using four amines.

Results:

Cu - Solubility decreased with increasing amounts of amines. A maximum decrease in copper from .034% to .016% was obtained with 2 lb. AM-Coco-C per ton ore,

NaCN - Consumption corresponded to copper solubility,

NaCN/Cu - Constant at 3,

CaO - Consumption increased with decrease in copper solubility.

Discussion of Results:

A possible explanation of the decrease in copper solubility, with the addition of amines, is the adsorption of the amines at the surface of the copper minerals to form an insoluble coating to cyanide solutions. With the addition of increasing amounts of the amine this coating becomes more effective. The possibility of the amine precipitating the copper as an insoluble compound appears doubtful, in that the concentrations

employed are small. For example, the maximum reduction in copper solubility from .034 to .016 per cent, equivalent to .0029 mols. of copper, is effected by .001 mols. of amine. This is less than a ratio of one mol. of amine per mol. of copper reduction and would appear to discredit the possibility of a precipitation reaction occurring.

Table 7. - Effect of Various Amines on the Solubility of Copper in the Cyanidation of a Copper Sulfide Ore

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	Amines added lb./ton Ore AM-1120	Copper in Soln. %	Mol. Ratio NaCN/Cu
158	.100-.0245	7.55	.025-.0290	-0.40	Nil	.034	2.9
190	.100-.0355	6.45	.025-.0320	-0.70	0.10	.032	2.6
191	.100-.0560	4.40	.025-.0285	-0.35	0.50	.020	2.9
192	.100-.0580	4.20	.025-.0275	-0.25	1.00	.018	3.0
193	.100-.0580	4.20	.025-.0260	-0.10	2.00	.018	3.0
					AM-Coco-C		
158	.100-.0245	7.55	.025-.0290	-0.40	Nil	.034	2.9
194	.100-.0335	6.65	.025-.0300	-0.50	0.10	.028	3.1
195	.100-.0505	4.95	.025-.0300	-0.50	0.50	.022	2.9
196	.100-.0570	4.30	.025-.0280	-0.30	1.00	.018	3.1
197	.100-.0610	3.90	.025-.0245	0.05	2.00	.016	3.2
					12NAM-1181.5C		
158	.100-.0245	7.55	.025-.0290	-0.40	Nil	.034	2.9
198	.100-.0285	7.15	.025-.0285	-0.35	0.10	.034	2.7
199	.100-.0325	6.75	.025-.0290	-0.40	0.50	.028	3.1
200	.100-.0375	6.25	.025-.0275	-0.25	1.00	.026	3.1
201	.100-.0420	5.80	.025-.0265	-0.15	2.00	.024	3.1
					AMAC-118.5C		
158	.100-.0245	7.55	.025-.0290	-0.40	Nil	.034	2.9
202	.100-.0295	7.05	.025-.0285	-0.25	0.10	.034	2.7
203	.100-.0325	6.75	.025-.0290	-0.40	0.50	.028	3.1
204	.100-.0375	6.25	.025-.0270	-0.20	1.00	.026	3.1
205	.100-.0450	5.50	.025-.0250	0.00	2.00	.022	3.2

INVESTIGATION No. 8. Effect of an amine (AM-Coco-C) on gold extraction, copper solubility, sodium cyanide consumption and lime consumption in the cyanidation of a pyrite and pyrite copper sulphide ore - Table 8 - Figs. 5 and 11.

As preliminary tests indicated that amines were effective in reducing copper solubility, a series of tests were run on a pyrite copper sulphide ore in which the addition of an amine (AM-Coco-C) was varied from 0.00 to 10.00 lb/ton ore.

Results:

Au - Extraction decreased rapidly from 48.7% to 8.3% with the addition of 1.00 pound of amine per ton ore. A slight increase to 15.3% extraction was obtained with the addition of 10.00 lb. of amine per ton ore.

Cu - Decreased in solubility from .034% to .016%

NaCN - Decreased in consumption from 7.90 to 5.50 lb. per ton ore.

Au/NaCN - Ratio decreased from 6.2 to 1.4 with a final slight increase to 2.8.

NaCN/Cu - Increased from 3.2 to 4.5

CaO - Increased in consumption comparable to the decrease in copper solubility.

Discussion of Results:

An examination of Table 8 indicates that with the addition of 2.50 lb. of amine the gold extraction is decreased 84% as compared to a decrease in copper solubility of 53%. The results indicate that if a differential actually exists for the adsorption of the amine on the copper minerals and gold, it would not be a favorable differential. The adsorption of the amine at the gold surface as in the case of copper forms and insoluble coating to cyanide solutions.

The amine additions in this investigation are not as effective in reducing copper solubility as in the cyanidation of the copper sulphide ore alone - Table 7. This may be attributed to the consumption of the amine by the pyrite ore, reducing the available amine concentrations for copper control.

The increase in the NaCN/Cu ratio is probably due to the introduction of a constant cyanide consumption by pyrite. With the decrease in total cyanide consumption, this constant appears larger, resulting in an increase in the NaCN/Cu ratio. The increased lime consumption is due to a partial consumption by pyrite in addition to the decreased formation of OH^- by copper dissolution.

Table 8. - Effect of an Amine (AM-Coco-C) on Gold Extraction, Copper Solubility, Sodium Cyanide Consumption and Lime Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulfide Ore.

Test No.	NaCN Range % Soln.	 Consump. lb./ton Ore	CaO Range % Soln.	 Consump. lb./ton Ore	Amine AM-Coco-C lb./ton Ore	Copper in Soln. %	Au Extraction Oz./ton Ore	Relative Au Extraction %	Mol. Ratio NaCN/Cu	Ratio Au/NaCN
214	.100-.0890	1.10	.025-.0160	0.90	Nil	Nil	.720	100.0	---	9.1
215	.100-.0210	7.90	.025-.0180	0.70	Nil	.032	.350	48.7	3.2	6.2
216	.100-.0235	7.65	.025-.0150	1.00	0.10	.030	.340	47.3	3.3	6.2
217	.100-.0525	6.75	.025-.0140	1.10	0.50	.026	.070	9.7	3.4	1.4
218	.100-.0405	5.95	.025-.0110	1.40	1.00	.020	.060	8.3	3.9	1.4
219	.100-.0425	5.75	.025-.0110	1.40	2.50	.016	.060	8.3	4.7	1.4
220	.100-.0455	5.45	.025-.0045	2.05	5.00	.016	.090	12.5	4.4	2.3
221	.100-.0450	5.50	.025-.0015	2.35	10.00	.016	.110	15.3	4.5	2.6

Test 214 was run as a standard test.

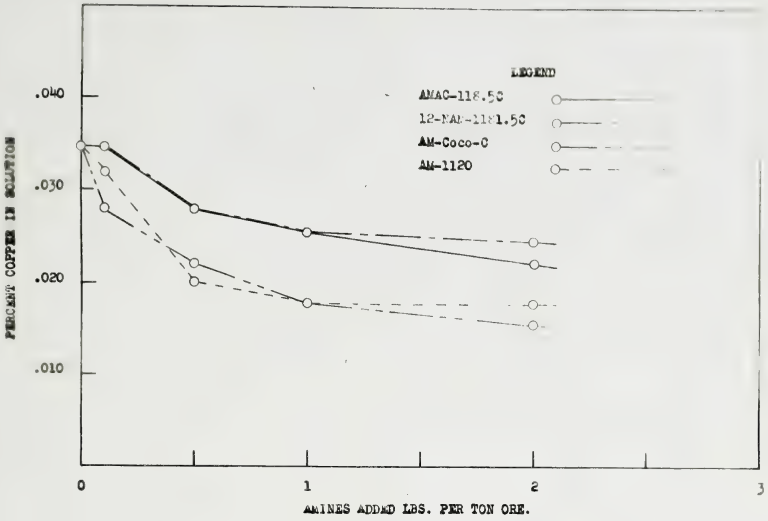

FIG. 4 EFFECT OF AMINES ON THE SOLUBILITY OF COPPER IN THE CYANIDATION OF A COPPER SULFIDE ORE.

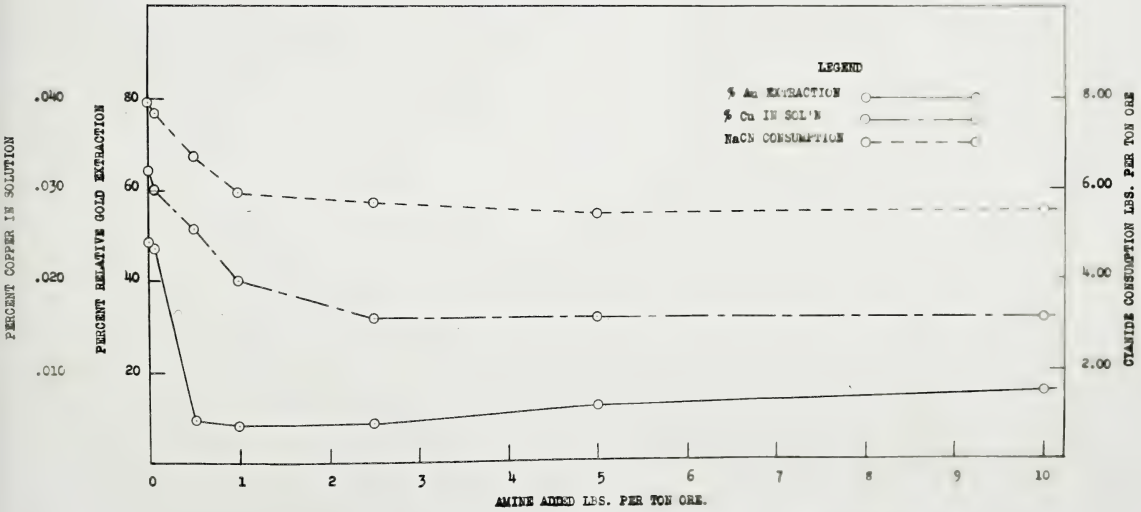

FIG. 5 EFFECT OF A AMINE (AM-Coco-C) ON THE RELATIVE GOLD EXTRACTION, COPPER SOLUBILITY, AND SODIUM CYANIDE CONSUMPTION IN THE CYANIDATION OF A PYRITE COPPER SULFIDE ORE.

INVESTIGATION No. 9. Effect of Xanthates and Stearic acid on the solubility of copper in the cyanidation of a copper sulphide ore - Table 9.

Tests were carried out on a copper sulphide ore in which the addition of ethyl xanthate, amyl xanthate and stearic acid respectively was varied from 0.00 to 5.00 lb. per ton ore.

Results:

Cu - Solubility constant for all three at .034%,

NaCN - Slight increase in consumption for the Xanthates. Constant for stearic acid,

NaCN/Cu - Constant at 3,

CaO - Constant consumption.

Discussion of Results:

The increased cyanide consumption with xanthates indicates a possible reaction between the xanthates and cyanide. The negative CaO consumption is due to the OH^- formation by copper dissolution, as explained in Investigation No. 5.

Table 9. - Effect of Xanthates and Stearic Acid on the Solubility of Copper in the Cyanidation of a Copper Sulphide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	Xanthate added lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
					Ethyl		
250	.100-.0225	7.75	.025-.029	-.40	Nil	.034	3.0
251	.100-.0225	7.75	.025-.030	-.50	.10	.034	3.0
252	.100-.020	8.00	.025-.028	-.30	.50	.034	3.1
253	.100-.019	8.10	.025-.030	-.50	1.00	.034	3.1
254	.100-.016	8.40	.025-.0295	-.45	3.00	.034	3.2
255	.100-.014	8.60	.025-.030	-.50	5.00	.036	3.1
					Amyl		
250	.100-.0225	7.75	.025-.029	-.40	Nil	.034	3.0
256	.100-.0215	7.35	.025-.030	-.50	.10	.032	3.2
257	.100-.0165	8.35	.025-.030	-.50	.50	.034	3.2
258	.100-.015	8.50	.025-.030	-.50	1.00	.034	3.2
259	.100-.0125	8.75	.025-.030	-.50	3.00	.034	3.3
260	.100-.0125	8.75	.025-.030	-.50	5.00	.036	3.2
			NaOH = CaO		Stearic Acid		
250	.100-.0225	7.75	.025-.029	-.40	Nil	.034	3.0
261	.100-.023	7.70	.025-.032	-.70	.10	.032	3.1
262	.100-.0255	7.45	.025-.0325	-.75	.50	.032	3.0
263	.100-.025	7.50	.025-.033	-.80	1.00	.034	2.9
264	.100-.023	7.70	.025-.033	-.80	3.00	.032	3.1
265	.100-.025	7.50	.025-.033	-.80	5.00	.034	2.9

INVESTIGATION No. 10. Effect of pH on the solubility of copper, using phosphates as a buffer reagent - Table 10- Fig. 6.

Tests were conducted on a copper sulphide ore in which the pH was varied by the addition of phosphates. The pH determinations were taken before and after agitation.

Results:

Cu - Solubility decreased from a value of 0.036% at pH 10.8 to 0.012% at pH 7.65, and then increased erratically when the pH was further lowered. The value of 0.018% Cu at pH 10.2 seemed out of line.

NaCN - Consumption increased to a maximum at pH 9.55, then decreased to a minimum at pH 7.65 followed by a final increase.

NaCN/Cu - Ratio increased to a maximum at pH 7.65. All values were higher than normally found for the corresponding copper percent at high pH.

pH - Tests run at high pH showed a decrease of pH during agitation. Tests performed at low pH showed an increase of pH during agitation.

Discussion of Results:

The overall copper decrease is due presumably to

the decreased dissociation of HCN when the pH is lowered. The initial increase of copper may be caused by activation by phosphates. The final increase is, at this time, unexplainable. The cyanide consumption decrease corresponds to the copper variation. However, because of the limited dissociation of HCN the values for cyanide consumption by copper are probably high as the titration of the "free cyanide" does not include all the undissociated HCN. Because of this the mol. ratio of cyanide to copper is found higher than normally found at high pH. From the values of pH prior to and after agitation, results indicated an acidifying action. It may be that the dissolved carbon dioxide from the air during agitation overrides the basic effect produced when the copper complex forms or that the phosphoric acid is incompletely dissolved when the initial pH determinations are taken.

Table 10. - Effect of pH on the Solubility of Copper, using phosphates as a Buffer Reagent, in the Cyanidation of a Copper Sulphide Ore

Test No.	NaCN Range % Soln.	 Consump. lb./ton Ore	Na_2HPO_4 lb./ton Soln.	H_3PO_4 lb./ton Soln.	pH Range	Copper in Soln. %	Mol. Ratio NaCN/Cu
296	.100-.0235	7.65	Nil	Nil	10.80-11.60	.036	2.8
297	.100-.0175	8.25	20	Nil	10.20-10.65	.018	6.0
298	.100-.0160	8.40	20	1.0	9.55-9.35	.038	2.9
299	.100-.0180	8.20	20	2.0	9.05-8.30	.024	4.4
300	.100-.0230	7.70	20	3.0	8.50-7.95	.019	5.3
301	.100-.0290	7.10	20	4.0	7.95-7.80	.017	5.4
302	.100-.0345	6.55	20	5.0	7.70-7.60	.015	5.7
303	.100-.0370	6.30	20	6.0	7.65-7.45	.012	6.8
304	.100-.0325	6.75	20	7.0	7.40-7.35	.021	4.2
305	.100-.0305	6.95	20	8.0	7.20-7.25	.018	5.0

INVESTIGATION No. 11. Effect of pH on the solubility of copper, using various buffer reagents, in the cyanidation of a copper sulphide ore - Table 11.

Tests were conducted on a copper sulphide ore in which the pH was varied by different buffers to determine if the variations of copper content were attributed to the pH change or the character of the buffer reagent.

Results:

Cu - Solubility decreased in the lowering of pH. The effect was the same using phosphate and acetate buffers but less pronounced with borax. This difference is especially so at low pH.

NaCN - Consumption decreased to a minimum at pH of 7.2 and then increased on further drop of pH.

NaCN/Cu - High values were obtained except in the case of borax.

pH - The pH values prior to agitation were higher than those obtained after agitation.

Discussion of Results:

The decrease in copper solubility appears to be primarily due to limited dissociation of HCN because of pH lowering, rather than to the character of the buffer salts. Some action of the borax salts encouraged HCN

dissociation even at low pH. The cyanide consumption seems high but is misrepresented on account of distorted titration. The consumption at pH's below 7 is comparatively higher than above 7 even though the copper dissolution is less. This is because the HCN becomes less dissociated as the pH is lowered, and gas losses by vaporization of the HCN are greater. As a result of the cyanide consumption appearing high, the cyanide copper ratios indicate high values. The decrease of pH during agitation indicate the same acidifing action as found in investigation No. 10.

Table 11. - Effect of pH on the Solubility of Copper, using Various Buffer Reagents, in the Cyanidation of a Copper Sulphide Ore

Test No.	Range % Soln.	Consump. lb./ton Ore	lb./ton Soln. Borax	lb./ton Soln.	pH Range	Copper in Soln. %	Mol. Ratio NaCN/Cu
271	.100-.0120	8.80	20	-	9.8-9.5	.034	3.4
272	.100-.0120	8.80	10	-	9.8-9.5	.036	3.2
273	.100-.0120	8.80	4	-	10.0-9.8	.034	3.4
290	.100-.0320	6.80	Na_2HPO_4 20	H_3PO_4 6	7.2-7.2	.017	4.8
291	.100-.0195	8.05	-	4	7.2-6.4	.013	8.05
292	.100-.0125	8.75	NaAC 20	HAC 2.6	7.2-6.3	.013	8.75
293	.100-.0030	9.70	-	2.5	7.2-5.6	.014	9.0
294	.100-.0170	8.30	Borax 2	Boric Acid 18	8.5-8.3	.034	3.2
295	.100-.0290	7.10	-	36	7.2-7.0	.020	4.6.

INVESTIGATION No. 12. Effect of pH on gold extraction and sodium cyanide consumption, using phosphates as a buffer reagent - Table 12 - Fig. 7.

So the dissolution rates of copper and gold with variation of pH might be compared, tests were conducted on a pyrite ore to establish the gold dissolution rate.

Results:

Cu - The gold dissolution decreased with lowering of pH, from a value of 114.1% relative recovery at pH 10.4 to a value of 57.8% relative recovery at pH 7.3,

NaCN - Consumption decreased slightly at a pH of 10.1 and then increased with decrease of pH.

Au/CN - This ratio reached a maximum at a pH of 10.1 and decreased with further lowering of pH.

Discussion of Results:

The decrease of gold dissolution is due to the decreased "effective" cyanide strength because of incomplete dissociation of HCN at low pH. The apparent anomaly of decreasing gold solubility and increasing cyanide consumption is attributed to the titration of the dissociated HCN and only part of the undissociated HCN. This accounts for the low gold cyanide ratios at low pH's.

From this investigation and Investigation No. 10 it is observed that copper solubility is limited to a greater extent than is the gold dissolution at low pH values. Over the range covered gold decreases 49.3% and copper drops 50% with a maximum drop of 66.7%. While a differential exists between the dissolution rates, it is thought not to be great enough to be of economic value.

Table 12. - Effect of pH on Gold Extraction and Sodium Cyanide Consumption, using Phosphates as a Buffer Reagent, in the Cyanidation of a Pyrite Ore

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	Na_2HPO_4 lb./ton Soln.	H_3PO_4 lb./ton Soln.	pH Range	Au Extr. Oz./ton Ore	Relative Au Extr. %	Ratio Au/CN
326	.100-.0950	0.50	--	---	11.4	.675	100.0	200
319	.100-.0835	1.65	--	---	10.70-10.15	.770	114.1	69
320	.100-.0915	0.85	20	---	10.10-9.95	.730	108.3	128
321	.100-.0860	1.40	20	1.0	9.60-9.40	.700	103.8	74
322	.100-.0840	1.60	20	2.0	9.05-8.90	.640	94.8	59
323	.100-.0775	2.25	20	3.0	8.50-8.30	.510	75.5	34
324	.100-.0690	3.10	20	4.0	8.00-7.85	.480	71.2	23
325	.100-.0555	4.45	20	7.0	7.30-7.20	.390	57.8	13

Test 326 was run in a lime cyanide solution as a standard test. CaO range 0.025-0.0155 per cent, CaO consumption 0.95 pounds per ton of Ore. Reducing power of solution for test 326 was 20. Reducing power of remaining tests was 18.

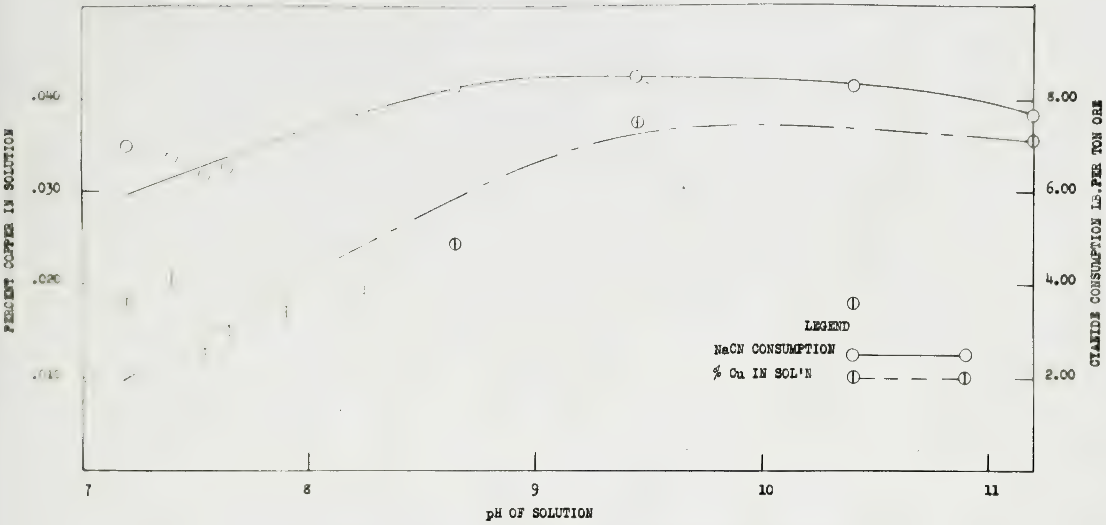

FIG. 6 EFFECT OF pH ON THE SOLUBILITY OF COPPER AND CYANIDE CONSUMPTION, USING PHOSPHATES AS A BUFFER REAGENT, IN THE CYANIDATION OF A COPPER SULPHIDE ORE.

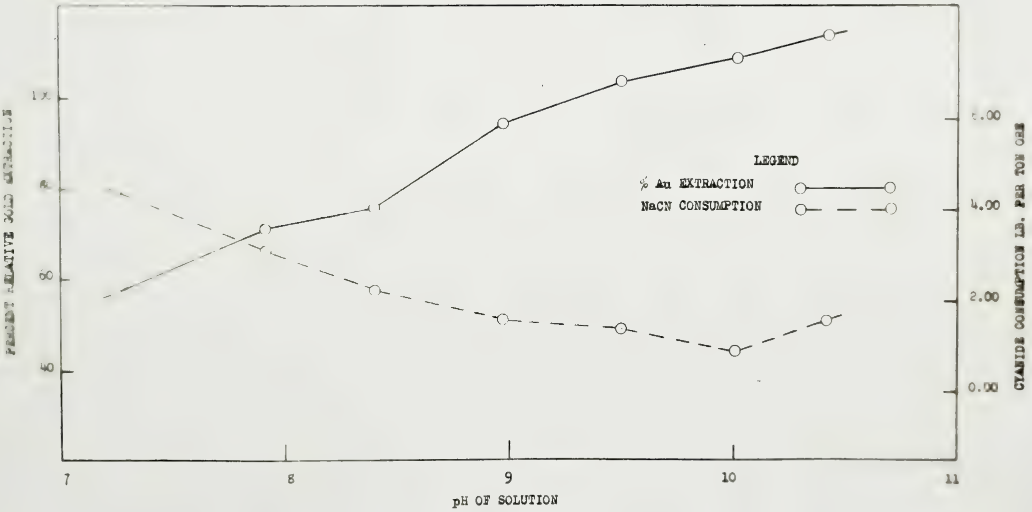

FIG. 7 EFFECT OF pH ON GOLD EXTRACTION AND SODIUM CYANIDE CONSUMPTION, USING PHOSPHATES AS A BUFFER REAGENT, IN THE CYANIDATION OF A PYRITE ORE.

INVESTIGATION No. 13. Effect of aluminum oxide on the solubility of copper - Table 13.

To determine if Al_2O_3 has any effect on copper solubility by oxidation, electrochemical action, or some other means, tests were performed on a copper sulphide ore in which different amounts of Al_2O_3 were added.

Results:

Cu - Solubility remained constant,

NaCN - There was no change in the cyanide consumption with increase of Al_2O_3,

NaCN/Cu - The ratio was found to be constant within experimental limitations. The average value was 3.06,

CaO - There was no significant change in alkalinity.

Discussion of Results:

Although literature records that Al_2O_3 is soluble in alkali solutions, it is thought that the cyanide solution is insufficiently alkaline to give an appreciable dissolution of Al_2O_3. Nevertheless, there are no indications that even if Al_2O_3 is soluble that it would retard the dissolution of copper.

Table 13. - Effect of Aluminum Oxide (Al_2O_3) on the Solubility of Copper in the Cyanidation of a Copper Sulfide Ore

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	Al_2O_3 added lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
120	.100-.0230	7.70	.025-.0290	-0.40	Nil	.032	3.1
127	.100-.0240	7.60	.025-.0310	-0.60	0.05	.028	3.5
128	.100-.0230	7.70	.025-.0290	-0.40	0.10	.032	3.1
129	.100-.0230	7.70	.025-.0270	-0.20	0.40	.034	2.9
130	.100-.0230	7.70	.025-.0210	0.40	0.70	.034	2.9
131	.100-.0240	7.60	.025-.0230	0.20	1.00	.034	2.9
137	.100-.0230	7.70	.025-.0290	-0.40	2.00	.034	2.9
138	.100-.0230	7.70	.025-.0290	-0.40	5.00	.032	3.1
139	.100-.0230	7.70	.025-.0285	-0.35	10.00	.032	3.1

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INVESTIGATION No. 14. Effect of PbO on the solubility of copper in a lime cyanide solution - Table 14-Fig. 8.

As PbO has been found to be an effective reagent in the cyanidation of gold ores other than cupriferous it was decided to study its effect when applied to cupriferous gold ores. Preliminary tests were conducted on a copper sulphide ore.

Results:

Cu - Solubility decreased from a value of 0.032% Cu to 0.006% Cu when the equivalent to 3 lb. per ton ore of PbO was added. Further addition of PbO failed to lower the copper %.

NaCN - Consumption dropped in parallel manner to that of copper solubility but not to the same extent. While the maximum decrease of copper was 81% the corresponding lowering of cyanide consumption was 75%.

NaCN/Cu - The overall effect was an erratic increase.

CaO - The consumption gave negative and positive values with a general trend from negative to positive.

Discussion of Results:

The reason for the decrease of copper in solution by addition of litharge is, at this time, not known. Because the cyanide consumption decreases, the inference

is that some of the complex copper ions are prevented from forming. This would eliminate the possibility of the copper complex ion being adsorbed on the PbO to a large extent. The assumption that copper combines with cyanide in the ratio of 1:3 does not appear valid when one considers the mol. ratio at low copper content. However, if there is a cyanide consumption not attributed to copper, then the assumption is not necessarily wrong. Also, such a consumption would be consistent with the increased mol. ratio at low copper concentrations. When calculations are made to determine this "extra" consumption the results vary from 0 to 1.95 lbs. per ton of ore, with an average value of 0.61. Variation is irregular and not consistent with copper change or PbO addition.

The foregoing phenomenon called for additional tests to determine if litharge alone consumed cyanide. For a range of 0 to 10 lbs. per ton ore of litharge the cyanide consumption by litharge was nil. Regardless, this does not rule out the possibility of indirect cyanide consumption by lead oxide when copper is present.

Table 14. - Effect of PbO on the Solubility of Copper in a Lime Cyanide Solution in the Cyanidation of a Copper Sulfide Ore.

Test No.	NaCN Range % Soln.	 Consump. lb./ton Ore	CaO Range % Soln.	 Consump. lb./ton Ore	PbO added lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
120	.100-.0230	7.70	.025-.029	-0.40	Nil	.032	3.1
121	.100-.0225	7.75	.025-.028	-0.30	0.05	.034	3.0
122	.100-.0215	7.85	.025-.033	-0.80	0.10	.032	3.2
123	.100-.0550	4.50	.025-.027	-0.20	0.40	.018	3.2
124	.100-.0600	4.00	.025-.027	-0.20	0.70	.014	3.7
125	.100-.0605	3.95	.025-.025	0.00	1.00	.010	5.1
132	.100-.0780	2.20	.025-.019	0.60	2.00	.008	3.6
133	.100-.0780	2.20	.025-.023	0.20	3.00	.006	4.8
134	.100-.0810	1.90	.025-.024	0.10	4.00	.006	4.1
135	.100-.0740	2.60	.025-.026	-0.10	5.00	.007	4.8
136	.100-.0805	1.95	.025-.026	-0.10	10.00	.006	4.2

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INVESTIGATION No. 15. Effect of lead acetate on the solubility of copper in a lime cyanide solution - Table 15, Fig. 8.

To further determine the effects and mechanisms by which lead salts decrease the solubility of copper, tests were run on a copper sulphide ore in which the variable was a soluble lead salt, namely, lead acetate.

Results:

Cu - Solubility decreased from a value of 0.034% Cu to 0.006% Cu when the equivalent to 10 lb. per ton ore of PbAc. was added.

NaCN - Consumption decrease parallels the copper decrease but not to the same extent. While the maximum decrease of copper was 82%, the corresponding lowering of cyanide consumption was 76%.

NaCN/Cu - Values obtained were irregular and showed no significant trend.

CaO - Consumption increased but not proportionate to the lead addition.

Discussion of Results:

Pound for pound the lead acetate is not as effective as litharge in limiting the copper solubility but is slightly better in reducing the cyanide consumption. However, to make a true comparison of the two reagents

it is necessary to reduce the respective amounts to molecular equivalents. The copper percentages and cyanide consumption are calculated on this basis and shown as follows:

Equiv. Amount	% Cu PbO	% Cu PbAc	NaCN Cons. PbO	NaCN Cons. PbAc
.1	.032	.028	7.85	7.20
.5	.017	.019	4.35	4.30
1	.010	.011	3.60	2.90
5	.007	.007	2.60	1.85
10	.006	.006	1.95	1.85

Comparison now shows little difference in copper percentages when equivalent amounts of litharge and lead acetate were added. This indicates that the lead radical, and not the non-metal radical is responsible for the reduction. For intermediate values, the acetate reduces the cyanide consumption to a greater extent than does the litharge. Presumably the non metal radical is an additional variable factor causing cyanide consumption. The choice between the use of litharge and lead acetate would be an ecomomic balance between the additional cost of acetate and the decreased cyanide cost.

The increased CaO consumption is accounted for by the decrease in copper solubility.

Table 15. - Effect of A Soluble Lead Salt, Lead Acetate, on the Solubility of Copper in the Cyanidation of a Copper Sulfide Ore.

	NaCN		CaO				
Test No.	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	PbAc added lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
158	.100-.0245	7.55	.025-.029	-0.40	Nil	.034	2.9
159	.100-.0260	7.40	.025-.030	-0.50	0.10	.028	3.4
160	.100-.0555	4.45	.025-.026	-0.10	0.50	.026	2.2
161	.100-.0695	3.05	.025-.024	0.10	1.00	.012	3.3
162	.100-.0815	1.85	.025-.016	0.90	5.00	.008	3.0
163	.100-.0820	1.80	.025-.012	1.30	10.0	.006	3.9

INVESTIGATION No. 16. Effect of lead silicate on the solubility of copper in a lime cyanide solution - Table 16 - Fig. 8.

Continuing the investigation of the effects of lead salts on copper solubility, tests were conducted on a copper sulphide ore in which the variable was an insoluble lead salt, namely, lead silicate.

Results:

Cu - Solubility remained constant until the equivalent of 10 lb. per ton ore of $PbSiO_3$ was added, when it decreased slightly.

NaCN - Consumption followed the same trend as the copper solubility.

NaCN/Cu - This ratio showed no significant variation.

CaO - Consumption stayed constant.

Discussion of Results:

The solubility of lead silicate is so low in the cyanide solutions that insufficient lead is supplied to affect the copper solubility.

Table 16. - Effect of Lead Silicate ($PbSiO_3$) on the Solubility of Copper in the Cyanidation of a Copper Sulfide Ore

Test No.	NaCN Range % Soln.	 Consump. lb./ton Ore	CaO Range % Soln.	 Consump. lb./ton Ore	$PbSiO_3$ added lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
242	.100-.0265	7.35	.025-.030	-0.50	Nil	.032	3.0
243	.100-.0265	7.35	.025-.030	-0.50	0.10	.034	2.8
244	.100-.0260	7.40	.025-.029	-0.40	0.30	.034	2.8
245	.100-.0260	7.40	.025-.029	-0.40	0.50	.032	3.0
246	.100-.0260	7.40	.025-.029	-0.40	0.80	.032	3.0
247	.100-.0265	7.35	.025-.029	-0.40	1.00	.032	3.0
248	.100-.0270	7.30	.025-.031	-0.60	5.00	.034	2.8
249	.100-.0335	6.65	.025-.030	-0.50	10.00	.030	2.9

INVESTIGATION NO. 17. Effect of PbO on gold extraction, copper solubility, sodium cyanide consumption and lime consumption in the cyanidation of a pyrite and pyrite copper sulphide Ore - Table 17- Fig. 9 - Fig. 11.

As lead salts gave the desired effect when applied to a copper sulphide ore, tests were conducted on a pyrite gold ore to determine the effect of litharge on gold dissolution. Additional tests were run on an ore that contained both copper and gold to note if the relationships established on the individual ores held true when the ores were combined.

Results:

Au - Au pyrite only- when two lbs. per ton ore of PbO was added, the relative gold extraction decreased to 61.0%,

Gold and copper - when no lead was added the relative Au extraction was 50.8%. Litharge additions of 0.3 to 2.00 lb. per ton ore increased the extraction, the maximum of 88.5% was at 0.50 lb. per ton ore. Extraction decreased with further increase of PbO.

Cu - Solubility decreased but decrease was only approx. half of decrease when pyrite was absent.

NaCN - Au pyrite only - consumption decreased.

Gold and copper - consumption increased slightly when 0.30 lb. per ton ore of PbO was added, then decreased with further addition.

NaCN/Cu - Ratio gradually increased,

Au/CN - Ratio changed similar to gold extraction but maximum found at 1.5 and 2.0 lb/ton ore.

CaO - Consumption erratic

Au pyrite only - showed a decreasing trend

Gold and Copper - slight increase was followed by a small decrease.

Discussion of Results:

When the litharge is added to the gold pyrite ore alone the gold dissolution decreases but not to the same extent as does the copper in Investigation No. 14. This is shown by the following table.

PbO	Au % Decrease	Cu % Decrease	Differential Cu/Au
0.50	4.4	47.0	10.6
1.00	28.3	68.8	2.4
2.00	39.0	75.0	1.9

Thus it is evident that small amounts of lead salts are more beneficial than large amounts. At low concentrations, the action of the lead salts seems similar to the action on the copper minerals but to a lesser extent. This suggests the mechanism of mineral coating.

When pyrite and copper minerals are agitated with no addition agents, the relative gold extraction drops to 50.8%. It is presumed that the gold extraction decrease has been attributed to cyanide depletion by copper. However, there are indications that the copper complex ion further decreases the gold dissolution by coating the gold. This is brought out when tests 144 and 146 are compared. The cyanide strength for test 146 is lowered to a greater degree than test 144. But the gold recovery for test 146 is higher than 144. It is clear, then, that cyanide depletion is not the only factor affecting the gold dissolution.

Test 146 differs from test 144 in that 0.3 lb. per ton ore of litharge is added to test 146. This suggests that PbO prevents the copper from coating the gold in some manner. The following mechanisms are advanced to explain the above results:

(1) Pb ions adsorb on gold

(2) Pb ions adsorb on copper minerals. These two functions account for the decrease in the solubility of gold and copper.

(3) Copper ions adsorb on gold. This indicates why the dissolution of gold in the presence of copper ions is hindered to a greater degree than can be predicted from cyanide depletion alone.

(4) Copper ions adsorb on or react with PbO or Pb ions. This shows how the lead salts decrease the effect of (3), i.e. when lead salts are added the copper ions now adsorb on or react with the lead in preference to adsorbing on the gold. The maximum gold extraction is obtained by the correct balance of all mechanisms. Too little lead does not fully utilize the advantages of (2) and (4) while too much lead by (1) nullifies the action of (2) and (4). This is nicely shown by table 17 and Fig. 9 when increase of PbO up to 0.50 lb. per ton ore gave the maximum extraction and further litharge increase reduced the extraction.

The general drop in cyanide consumption is consistent with the decreased solubility of copper. The small increased consumption at low amounts of litharge presents an interesting, but, at this time, unexplainable variation. The increase in mol. ratio is consistent when one considers that the cyanide consumption by the pyrite is not deducted from the total cyanide consumption when calculating this ratio. As there is no reason to believe that this consumption by pyrite should be constant, the interpretion of the molecular ratio, when the consumption by pyrite is deducted, might lead to faulty deductions. The maximum gold cyanide ratio has

economic significance when one wishes to obtain gold extraction with minimum cyanide consumption. The choice between maximum gold extraction and maximum gold cyanide ratio is a balance between the price of gold and the cost of cyanide.

Table 17. - Effect of PbO on Gold Extraction, Copper Solubility, Sodium Cyanide Consumption and Lime Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	PbO added lb./ton Ore	Copper in Soln. %	Gold Extraction Oz./ton Ore	Relative Au Extraction %	Mol. Ratio NaCN/Cu	Ratio Au/NaCN
140	.100-.0810	1.90	.025-.0060	1.90	Nil	Nil	.690	100.0	---	53
141	.100-.0805	1.95	.025-.0130	1.20	0.50	Nil	.660	95.6	---	49
142	.100-.0840	1.60	.025-.0125	1.25	1.00	Nil	.495	71.7	---	45
143	.100-.0835	1.65	.025-.0130	1.20	2.00	Nil	.420	61.0	---	37
144	.100-.0190	8.100	.025-.0210	0.40	Nil	.032	.350	50.8	3.3	6.3
145	.100-.0180	8.20	.025-.0210	0.40	0.10	.032	.345	50.0	3.3	6.1
146	.100-.0175	8.25	.025-.0210	0.40	0.30	.032	.550	79.7	3.3	9.9
147	.100-.0215	7.35	.025-.0190	0.60	0.50	.028	.610	88.5	3.6	11.3
148	.100-.0230	7.70	.025-.0190	0.60	0.70	.026	.520	75.4	3.8	9.8
149	.100-.0290	7.10	.025-.0220	0.30	1.00	.026	.530	76.8	3.5	10.9
150	.100-.0360	6.40	.025-.0180	0.70	1.50	.024	.570	82.6	3.5	12.9
153	.100-.0505	4.95	.025-.0205	0.45	2.00	.016	.420	61.0	4.0	12.3
154	.100-.0555	4.45	.025-.0205	0.45	3.00	.012	.220	31.9	4.8	7.2
155	.100-.0635	3.65	.025-.0185	0.65	4.00	.008	.130	18.9	5.9	5.2
156	.100-.0635	3.65	.025-.0205	0.45	5.00	.006	.090	13.0	7.9	3.6
157	.100-.0635	3.65	.025-.0185	0.65	10.00	.006	.050	7.3	7.9	2.0

Test 140 was run as a standard test.

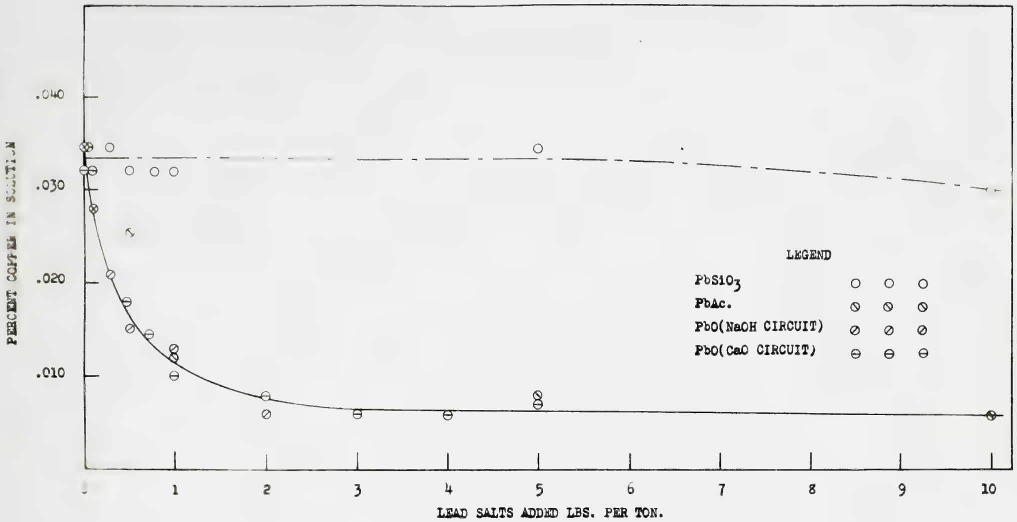

FIG. 8 EFFECT OF VARIOUS LEAD SALTS ON THE SOLUBILITY OF COPPER IN THE CYANIDATION OF A COPPER SULFIDE ORE.

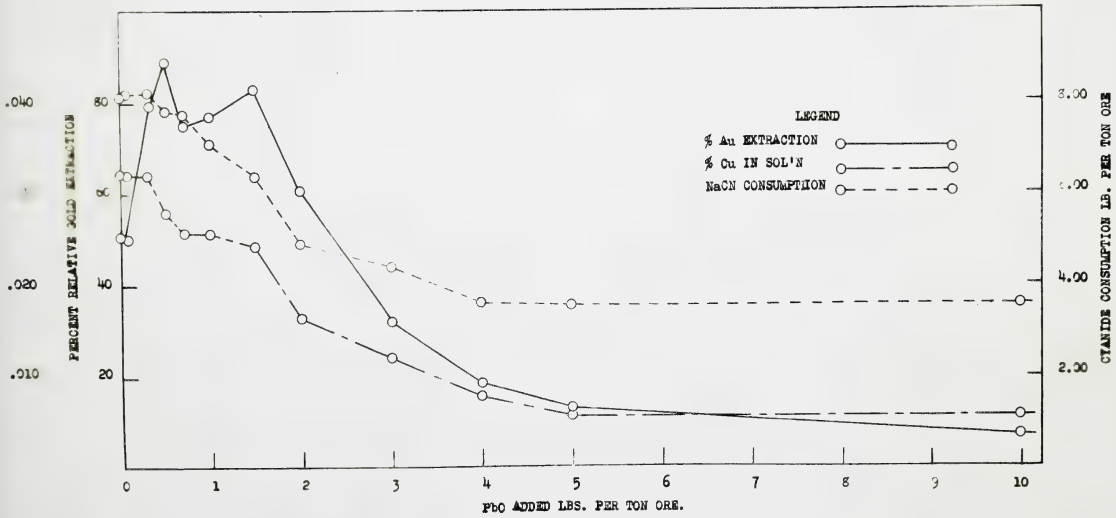

FIG. 9 EFFECT OF PbO ON RELATIVE GOLD EXTRACTION, COPPER SOLUBILITY, AND SODIUM CYANIDE CONSUMPTION, IN A LIME CYANIDE SOLUTION, IN THE CYANIDATION OF A PYRITE COPPER SULFIDE ORE.

INVESTIGATION No. 18   Effect of PbO on the solubility of copper in a sodium hydroxide cyanide solution - Table 18, Fig. 8.

Tests were performed on a copper sulphide ore in a sodium hydroxide circuit to determine if the character of the alkali influenced the mechanism by which litharge lowered the copper solubility.

Results:

Cu - Solubility decrease from a value of 0.032% Cu to 0.006% Cu when litharge to the equivalent to 2 lb. per ton ore was added.

NaCN - Consumption decrease paralled the copper solubility lowering but not to the same degree. The maximum decrease of copper was 82%, the corresponding lowering of cyanide consumption was 68%.

NaCN/Cu - The overall effect was an erratic increase.

CaO - The general trend was an increasing consumption.

Discussion of Results:

The following table gives a comparison of the action of litharge on the copper solubility in CaO and NaOH circuits.

PbO lb/T. ore	NaOH Circuit % Cu	CaO Circuit % Cu
nil	0.034	0.032
0.10	0.028	0.032
0.30	0.021	0.023
0.50	0.015	0.017
1.00	0.013	0.010
2.00	0.006	0.008

While the overall picture tends to show that PbO is more effective in a NaOH circuit, the variation in individual values does not warrant a definite conclusion to this relationship. Comparison of cyanide consumption, cyanide copper ratios, and alkali consumptions does not add anything more to establishing that PbO is more effective in a sodium hydroxide circuit.

No additional information that might aid in establishing fundamental relationships is obtained by conducting this test. Therefore, a detailed analysis of copper solubilities, cyanide consumptions, copper cyanide ratios, and alkali consumptions, would be of no value.

Table 18. - Effect of PbO on the Solubility of Copper in Sodium Hydroxide Cyanide Solution in the Cyanidation of a Copper Sulfide Ore

	NaCN		NaOH ≡ CaO				
Test No.	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	PbO added lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN / Cu
164	.100-.0260	7.40	.025-.0310	-0.60	Nil	.034	2.8
165	.100-.0255	7.45	.025-.0260	-0.10	0.10	.028	3.5
166	.100-.0420	5.80	.025-.0250	0.00	0.30	.021	3.6
167	.100-.0610	3.90	.025-.0205	0.45	0.50	.015	3.4
168	.100-.0655	3.45	.025-.0210	0.40	1.00	.013	3.4
169	.100-.0765	2.35	.025-.0230	0.20	2.00	.006	5.1

INVESTIGATION No. 19. Effect of PbO on gold extraction copper solubility, and sodium hydroxide consumption in the cyanidation of a pyrite and pyrite copper sulphide ore-Table 19, Fig. 10, Fig. 11.

Tests were performed on a pyrite gold ore to determine if the effectiveness of litharge changes when the type of alkalinity is varied. Further tests were run on a gold and copper ore to note if the trends found in the tests on the individual ores held true when the ores were combined.

Results:

Au - Au pyrite only - Up to 2 lb. PbO per ton ore, the dissolution of gold showed no significant change, On the addition of 5 lb. PbO per ton ore the Au extraction dropped to 47.0%.

Gold and copper - When no lead was added, the relative Au extraction was 57.6%. Addition of PbO up to 3.0 lb. per ton ore increased the extraction, with maximum of 104.5% at 1.0 lb. PbO per ton ore.

Cu - Solubility decreased but decrease was only approx. 1/3 of decrease when pyrite was absent.

NaCN - Au pyrite only - consumption decreased

gold and copper - consumption increased when 0.30 lb. per ton ore of PbO added, then decreased with further addition.

NaCN/Cu - Ratio gradually increased,

Au/CN - Ratio changed in a manner similar to variation of gold extraction,

CaO - consumption variation erratic,

Au pyrite only - showed a decreasing trend

gold and copper - variation too erratic to show any trend.

Discussion of Results:

The following table shows an interesting difference in the gold extraction when tests performed on a gold pyrite ore only, were conducted in lime and sodium cyanide solutions.

PbO	% Au Extraction in CaO Circuit	% Au Ext'n. NaOH Circuit
0.00	100	110.6
0.50	95.6	116.6
1.00	71.7	110.6
2.00	61.0	112.1
5.00	-----	47.0

The gold is not coated as effectively by lead in a NaOH circuit as in a lime circuit. The higher value for gold extraction, when no litharge is present for the NaOH circuit substantiates the experimental evidence of other investigators that lime is detrimental to gold dissolution. The ability of lead to coat gold now seems to be a function of the type of alkali in solution. Comparison of the copper dissolution values in both

type of alkalis shows that this dependency of the lead coating ability on the type of alkali extends to the copper minerals. For this reason the maximum gold extraction is shifted to 1.0 lb. per ton ore of PbO. Because of the absence of the detrimental effect of CaO, the gold cyanide ratios are higher for the NaOH circuit than the corresponding values in the lime circuit.

Table 19. - Effect of PbO on Gold Extraction, Copper Solubility, Sodium Cyanide Consumption and Sodium Hydroxide Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	NaOH - CaO Range % Soln.	NaOH - CaO Consump. lb./ton Ore	PbO added lb./ton Ore	Copper in Soln. %	Au Extraction Oz./ton Ore	Relative Au Extraction %	Mol. Ratio NaCN/Cu	Ratio Au/NaCN
222	.100-.0890	1.10	.025-.0110	1.40	Nil	Nil	.660	100.0	---	91
174	.100-.0810	1.90	.025-.0120	1.30	Nil	Nil	.730	110.6	---	58
175	.100-.0830	1.70	.025-.0200	0.50	0.50	Nil	.770	116.6	---	69
176	.100-.0835	1.65	.025-.0210	0.40	1.00	Nil	.730	110.6	---	67
177	.100-.0860	1.40	.025-.0210	0.40	2.00	Nil	.740	112.1	---	80
178	.100-.0890	1.10	.025-.0205	0.45	5.00	Nil	.310	47.0	---	43
179	.100-.0230	7.70	.025-.0300	-0.50	Nil	.034	.380	57.6	2.9	7.5
180	.100-.0210	7.90	.025-.0305	-0.55	0.10	.034	.380	57.6	3.0	7.3
181	.100-.0160	8.40	.025-.0330	-0.80	0.30	.032	.540	81.8	3.4	9.7
182	.100-.0200	8.00	.025-.0300	-0.50	0.50	.030	.480	72.7	3.5	9.1
183	.100-.0230	7.70	.025-.0300	-0.50	0.70	.028	.420	63.7	3.6	8.3
184	.100-.0375	6.25	.025-.0265	-0.15	1.00	.026	.690	104.5	3.1	16.7
185	.100-.0310	6.90	.025-.0310	-0.60	2.00	.024	.630	95.5	3.7	13.8
186	.100-.0530	4.70	.025-.0280	-0.30	3.00	.013	.510	77.3	4.7	16.4
187	.100-.0540	4.60	.025-.0270	-0.20	4.00	.013	.340	51.6	4.6	11.2
188	.100-.0635	3.65	.025-.0275	-0.25	5.00	.010	.190	28.8	4.7	7.9
189	.100-.0650	3.50	.025-.0270	-0.20	10.00	.008	.100	15.2	5.7	4.3

Test 222 was carried out in a lime cyanide solution as a standard with which to compare the other tests which were run in a sodium hydroxide cyanide solution.

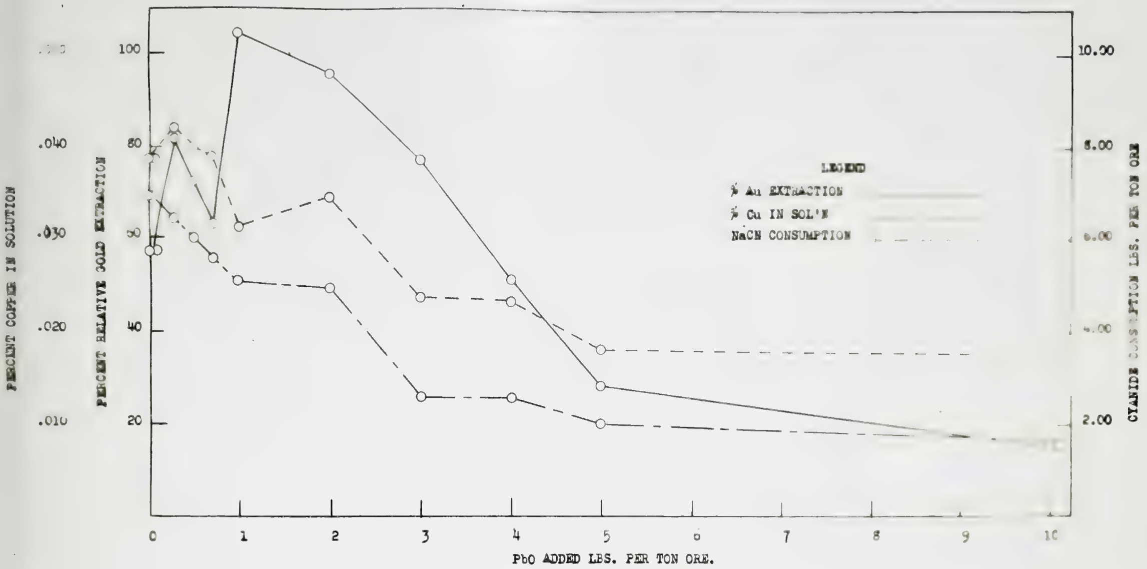

FIG. 10 EFFECT OF PbO ON RELATIVE GOLD EXTRACTION, COPPER SOLUBILITY, AND SODIUM CYANIDE CONSUMPTION, IN A SODIUM HYDROXIDE CYANIDE SOLUTION, IN THE CYANIDATION OF A PYRITE COPPER SULFIDE ORE.

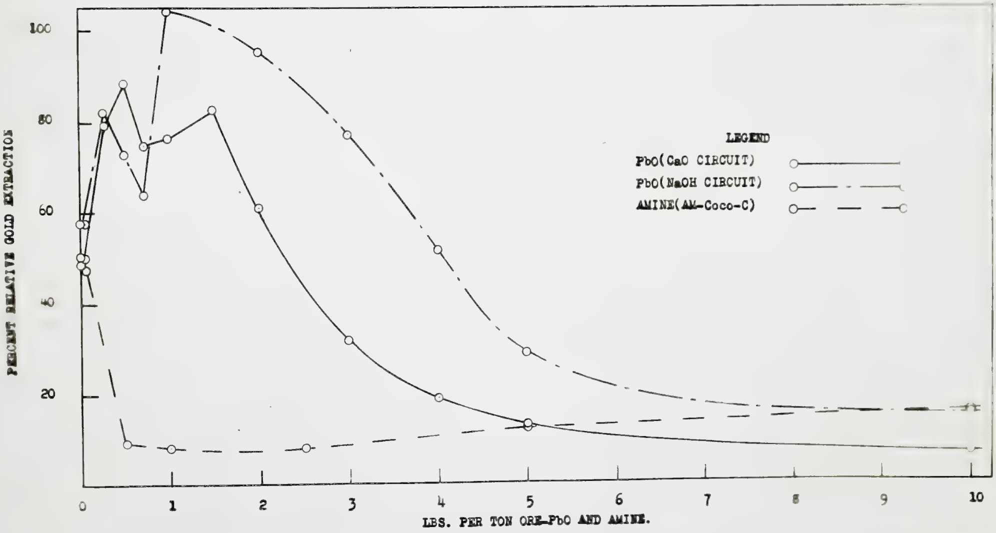

FIG. 11 EFFECT OF PbO IN A LIME CYANIDE SOLUTION, PbO IN A SODIUM HYDROXIDE CYANIDE SOLUTION AND AN AMINE(AM-Coco-C) IN A LIME CYANIDE SOLUTION, ON THE RELATIVE GOLD EXTRACTION IN THE CYANIDATION OF A PYRITE COPPER SULFIDE ORE.

INVESTIGATION No. 20. Effect of PbO in different alkaline cyanide solutions on gold extraction, copper solubility, cyanide consumption and alkali consumption in the cyanidation of a pyrite copper sulphide ore. Table 20, Fig. 12.

Tests were performed on a pyritic copper sulphide ore to substantiate the results obtained from investigations No. 17 and No. 19. Additional tests were run, in which no alkali was added to determine if alkali was necessary when litharge was used to promote gold extraction in presence of copper minerals. So that the litharge would be more homogeneous, it was screened and only the -200 mesh product used.

Results:

Au - CaO circuit- The extraction trend was similar to that of investigation No. 17. At high values of PbO the decrease of recovery was greater than those reported in Investigation No. 17.

NaOH circuit - The extraction trend was similar to that of investigation No. 19. The actual values in this investigation were lower than the corresponding values in Investigation No. 19. The maximum recovery in this investigation was found at 0.5 lb. per ton ore PbO.

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

No alkali circuit - The extraction increased from a value of 50.7% when no lead was added, to maximum of 79.1% when 1.0 and 2.0 lb. per ton ore of PbO was added.

Cu - CaO circuit - solubility decreased from 0.034% to o.010% Cu when 2.0 lb. per ton ore of PbO was added. These values were lower than corresponding values determined in Investigation No. 17.

NaOH circuit - solubility dropped from 0.034% to 0.014% Cu when 2.0 lb. per ton ore of PbO was added. These values were lower than the corresponding values determined in Investigation No. 19.

No alkali circuit - solubility decreased from 0.032% to 0.028% Cu when 2.0 lb. per ton ore of PbO was added.

NaCN - CaO circuit - consumption was lowered to a greater degree than the corresponding values determined in Investigation No. 17.

NaOH circuit - consumption was lowered to a greater degree than the corresponding values determined in Investigation No. 19.

No alkali circuit - consumption increased slightly and then decreased to a small degree when PbO was added.

NaCN/Cu - CaO circuit - Ratio increased similar to values found in investigation No. 17.

NaOH circuit - Ratio increased similar to values found in Investigation No. 19.

No alkali circuit - No significant change was noted.

Au/CN - CaO circuit - trend similar to that of Investigation No. 17. Corresponding values for this investigation were higher than those of Investigation No. 17.

NaOH circuit - trend similar to that of Investigation No. 19.

No alkali circuit - values of ratio increased from 6.6 to 11.2 as PbO was added.

Alkali consumption - CaO circuit - values were erratic and no significant trend was observed.

NaOH circuit - a slight tendency for increasing alkalinity was noted.

No alkali circuit - consumption was negative, with the trend for the consumption values to become less negative.

pH - CaO circuit - values decreased from 11.80 to 11.70 as PbO was added.

NaOH circuit - values remained constant

at 11.70

No alkali circuit - values remained constant at 11.15,

R.P. CaO circuit - values decreased from 102 to 44,

NaOH circuit - values decreased from 94 to 56,

No alkali circuit - values decreased from 96 to 84.

Discussion of Results:

The results obtained from these tests do not conflict with the relationships established by Investigations No. 17 and 19. The greater effectiveness of the litharge in this investigation is attributed to the litharge being in a more finely divided state because of screening.

This investigation established the dependency of the litharge action on the type and degree of alkalinity. The following table is calculated to facilitate comparisons of each type.

Type of Alkali	% Au Extr. Increase	% Cu Sol. Decrease	% CN Cons. Decrease	pH
No alkali	56	13	8	11.15
NaOH	92	59	43	11.70
CaO	75	71	58	11.75

The variation in results for lime and sodium hydroxide is attributed to the type of alkali (cf. Investigation

No. 19). It is suggested that because of the amphoteric nature of litharge, its solubility and effectiveness is increased by increase of pH. This would account for the difference in values between the no alkali circuit, and the lime and sodium hydroxide circuits.

The decrease in reducing power as litharge is added infers that litharge is an oxidizing agent in cyanide solutions, or that as the copper dissolves, the solution becomes of a reducing nature and litharge, by decreasing the copper solubility, appears as an oxidizing agent.

Table 20. - Effect of PbO in Different Alkaline Cyanide Solutions (CaO, NaOH and no alkali added) on Gold Extraction, Sodium Cyanide Consumption, Copper Solubility and Alkali Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore.

	NaCN		Alkalinity									
Test No.	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	pH	PbO added lb./ton Ore	R.P.	Cu in Soln. %	Mol. Ratio NaCN/Cu	Au Extr. Oz./ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
			CaC									
338	.100-.0935	0.65	.025-.0190	0.60	11.60	Nil	14	Nil		.670	100.0	154
339	.100-.0225	7.75	.025-.0260	-0.10	11.80	Nil	102	.034	3.0	.320	47.7	6.2
340	.100-.0390	6.10	.025-.0270	-0.20	11.80	0.50	92	.024	3.05	.560	83.5	13.5
341	.100-.0500	5.00	.025-.0260	-0.10	11.75	1.00	76	.020	3.25	.500	74.6	14.9
342	.100-.0550	4.50	.025-.0270	-0.20	11.75	1.50	64	.018	3.25	.300	44.8	10.0
343	.100-.0675	3.25	.025-.0255	-0.05	11.70	2.00	44	.010	4.2	.205	30.6	9.4
			NaOH									
344	.100-.0275	7.25	.025-.0260	-0.10	11.75	Nil	94	.034	2.8	.325	46.5	6.7
345	.100-.0410	5.90	.025-.0270	-0.20	11.70	0.50	90	.026	2.95	.625	93.3	15.5
346	.100-.0470	5.30	.025-.0260	-0.10	11.70	1.00	74	.020	3.4	.410	61.1	11.5
347	.100-.0555	4.45	.025-.0240	0.10	11.70	1.50	66	.018	3.2	.475	70.9	15.9
348	.100-.0590	4.10	.025-.0240	0.10	11.70	2.00	56	.014	3.8	.450	67.1	16.4
349	.100-.0235	7.65	.000-.006	-0.60	11.15	Nil	92	.032	3.1	.340	50.7	6.6
350	.100-.0225	7.75	.000-.009	-0.90	11.15	0.50	96	.030	3.35	.460	68.6	8.8
351	.100-.0235	7.65	.000-.008	-0.80	11.15	1.00	96	.030	3.3	.530	79.1	10.4
352	.100-.0270	7.30	.000-.008	-0.80	11.15	1.50	88	.030	3.2	.520	77.6	10.6
353	.100-.0295	7.05	.000-.007	-0.70	11.15	2.00	84	.028	3.3	.530	79.1	11.2

Test 338 was run in a lime cyanide solution as a standard test.
No alkali was added in tests 349 to 353.

INVESTIGATION NO. 21. Effect of varying NaOH with added PbO on gold extraction, copper solubility, sodium cyanide consumption and sodium hydroxide consumption in the cyanidation of a pyrite and pyrite copper sulphide ore - Table 21, Fig. 13.

Investigation No. 20 established that the effectiveness of litharge was dependent upon the degree of alkalinity, but did not establish where the optimum degree of alkalinity was. Additional tests were performed on a pyrite copper sulphide ore to determine the optimum for NaOH alkalinity. The NaOH concentration was varied from 0.015 to 0.150 per cent, using the optimum PbO of 0.50 lb. per ton ore, as determined from previous test work.

Results:

Au - extraction increased gradually to a maximum of 92.8% at 0.50% NaOH. Further increase in alkalinity resulted in a decreased extraction.

Cu - solubility decreased slightly from 0.030% to 0.024% Cu.

NaCN - consumption decreased from 7.60 to 5.50 lb. per ton ore at 0.075% NaOH. Further increase in alkalinity at 0.150% NaOH resulted in a slight increase in consumption

to 6.00 lb. per ton ore.

Au/NaCN - increased from 11.0 to maximum of 19.3, coincident with maximum gold recovery, then decreased to 14.2,

NaCN/Cu - constant

NaOH - consumption increased rapidly from -.030 to 1.35 lb. per ton ore.

pH - increased from 11.50 to 12.05,

R.P. - erratic results, varied from 112 to 96.

Discussion of results:

A maximum gold extraction of 92.8 per cent is obtained at .050% NaOH, however, alkalinity does not appear too critical a factor with respect to gold recovery. The Au/NaCN ratio with a maximum value of 19.3, coincident with maximum gold extraction, is more critical, showing an increase of 75% with increase in alkalinity of .015 to .050 per cent NaOH.

The decrease in copper solubility with increased alkalinity would appear to substantiate previous test work, which indicates that alkalinity is essential in affecting a reduction in copper solubility by coating with lead compounds. The increased NaOH consumption can be attributed to the decreased formation of OH^- with copper dissolution.

The decrease in cyanide consumption is consistent with copper solubility, as indicated by the constant NaCN/Cu ratio. The erratic results obtained for reducing power prevents its correlation with other factors.

Table 21. - Effect of Varying NaOH with added PbO on Gold Extraction, Copper Solubility, Sodium Cyanide Consumption and Sodium Hydroxide Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore.

	NaCN		NaOH=CaO									
Test No.	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	pH	PbO added lb./ton Ore	R.F.	Cu in Soln. %	Mol. Ratio NaCN/Cu	Au Extr. Oz./ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
359	.100-.0910	0.90	.025-.0170	0.80	11.60	Nil	16	Nil	--	.700	100.0	111
375	.100-.0240	7.60	.015-.0180	-0.30	11.50	0.50	112	.030	3.3	.585	83.6	11.0
376	.100-.0320	6.80	.025-.0265	-0.15	11.65	0.50	100	.0260	3.4	.575	82.2	12.1
377	.100-.0315	6.85	.035-.0355	-0.05	11.75	0.50	112	.028	3.2	.620	88.6	12.9
378	.100-.0420	5.80	.050-.0480	0.20	11.85	0.50	96	.024	3.15	.650	92.8	19.3
379	.100-.0445	5.55	.075-.0700	0.50	11.95	0.50	96	.024	3.0	.550	78.6	17.3
380	.100-.0400	6.00	.150-.1365	1.35	12.05	0.50	104	.024	3.25	.595	85.0	14.2

Test 359 was run in a lime cyanide solution as a standard test.

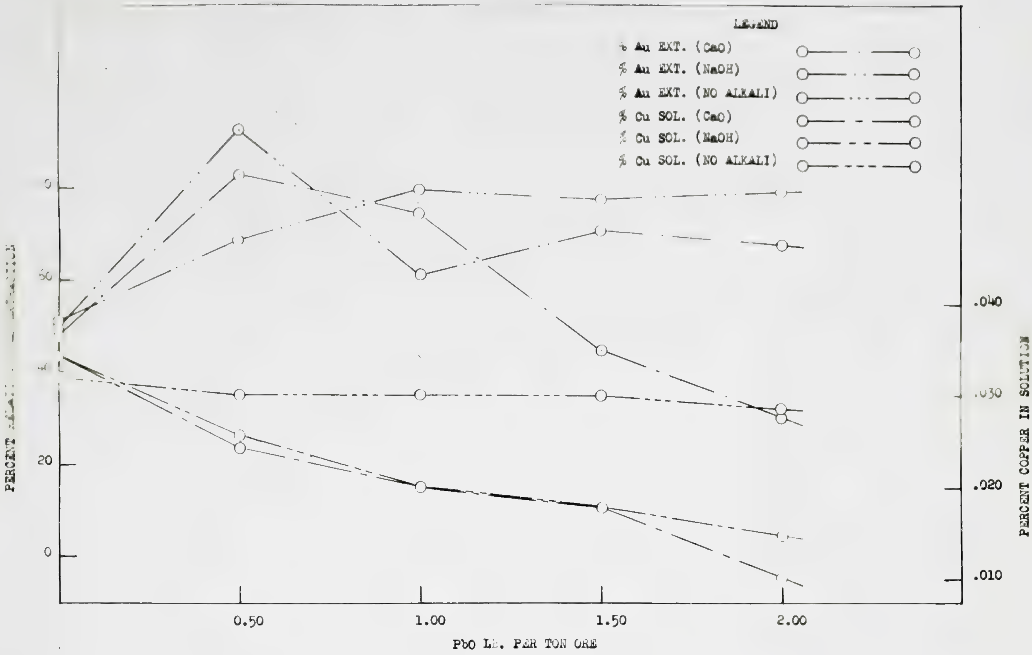

FIG. 12 EFFECT OF PbO IN DIFFERENT ALKALINE CYANIDE SOLUTIONS (CaO, NaOH, AND NO ALKALI) ON GOLD EXTRACTION AND COPPER SOLUBILITY IN THE CYANIDATION OF A PYRITE COPPER SULPHIDE ORE.

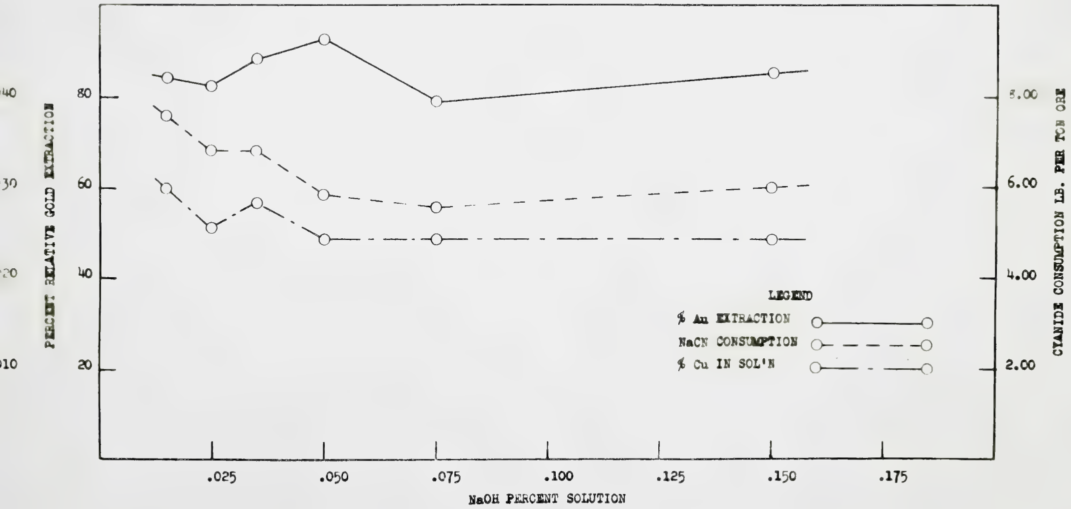

FIG. 13 EFFECT OF VARYING NaOH, WITH ADDED PbO, ON GOLD EXTRACTION, COPPER SOLUBILITY, AND SODIUM CYANIDE CONSUMPTION, IN THE CYANIDATION OF A PYRITE COPPER SULPHIDE ORE.

INVESTIGATION No. 22. Effect of PbO and varying sodium cyanide strength on gold extraction, copper solubility, sodium cyanide consumption and lime conconsumption in the cyanidation of a pyrite and pyrite copper sulphide ore - Table 22 - Fig. 14, Fig. 15.

To determine whether a differential existed between gold extraction and copper solubility (with and without PbO) with varying cyanide strength, tests were carried out on a pyrite ore, pyrite copper sulphide ore, and pyrite copper sulphide ore with added PbO. Cyanide strengths of .025, .050, .075 and .100 per cent were employed and the optimum PbO of 0.50 lb. per ton, as determined from previous test work, was used.

Results:

Au - Pyrite ore - extraction increased from 77.7% to 100.0%,

Pyrite Cu Ore - extraction increased from 18.1% to 47.3%,

Pyrite Cu ore + PbO - extraction increased from 23.6% to 79.2% with increased cyanide strength,

Cu - Pyrite Cu ore - solubility increased proportionately with cyanide strength from .008% .032%,

Pyrite Cu ore + PbO - solubility increased proportionately with cyanide strength from

.006% to .026%,

NaCN - Pyrite ore - consumption increased from 0.70 to 1.60 lb. per ton ore,

Pyrite Cu Ore - consumption increased from 2.20 to 8.15 lb. per ton ore,

Pyrite Cu ore $\not-$ PbO - Consumption increased from 2.30 to 7.50 lb. per ton ore.

Au/NaCN - Pyrite ore- maximum value 111 at .025% NaCN,

Pyrite Cu ore - maximum value 8.8 at .050% NaCN,

NaCN/Cu - Pyrite Cu ore - erratic, ranged from 3.3 to 4.1,

Pyrite Cu ore $\not-$ PbO - decreased from 5.0 to 3.7,

CaO - pyrite ore - consumption decreased from 1.20 to 0.85 lb. per ton ore.

Pyrite Cu ore - consumption decreased from 0.85 to -0.30 lb. per ton ore,

Pyrite Cu ore $\not-$ PbO - consumption decreased from 0.75 to -0.30 lb. per ton ore.

Discussion of Results:

An examination of the solubility of copper with cyanide strength, Investigation No. 4, and the dissolution of gold alone with cyanide strength, above,

indicates that an optimum differential exists at a cyanide strength of .025%.

NaCN Strength	% Cu	% Au	Differential Au/Cu
.025	25	77.7	3.1
.050	50	83.3	1.7
.075	75	98.6	1.3
.100	100	100.0	1.0

This becomes apparent when it is noted that copper solubility is almost directly proportional to cyanide concentration, whereas, gold dissolution increases rapidly at first with a gradual levelling off at higher cyanide concentrations. The Au/NaCN ratio, Fig. 15, for the dissolution of gold and copper together illustrates that the optimum differential now prevails at a cyanide strength of .050%. Upon the addition of PbO this differential increases and optimum conditions become less critical, operating over a cyanide strength range of .050% to .075%. The curves on gold extraction, Fig. 14 effectively illustrate the detrimental results of copper in cyanidation and the counteracting force of PbO.

The apparent decrease in CaO consumption with increase in cyanide strength, for the pyrite ore, may be attributed to the increase in OH^- concentration with increased CN^- concentration, since the OH^- and CN^-

ions are interdependent. In the cyanidation of the copper sulphide ore this decrease in CaO consumption is further accentuated by the dissolution of copper to form an additional OH^- ion concentration.

As previously mentioned the reason for the decrease in gold extraction when cyaniding the pyrite copper ore may be attributed to two causes: insufficient cyanide to dissolve gold, because of high consumption by copper; and alteration of the surface of gold by copper in such a way as to prevent cyanide from attacking the gold. Experimental work substantiates the latter point. In the cyanidation of the pyrite ore, test No. 230, cyanide strength ranging between 0.025% - 0.018%, a gold recovery of 77.7% is obtained. However, in the cyanidation of the pyrite copper ore, test No. 237, cyanide strength ranging between 0.100 - 0.018 per cent, a recovery of only 47.3% is obtained. It seems therefore, that the drop in gold extraction can be attributed in part to the copper. It is reasonable to suppose that the copper ions in solution are adsorbed on the surface of gold, forming a coating which is less easily attacked by cyanide than gold in its original state, thereby decreasing its rate of dissolution.

Table 22. - Effect of PbO and Varying Sodium Cyanide Strength on Gold Extraction, Copper Solubility, Sodium Cyanide Consumption and Lime Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulfide Ore.

	NaCN		CaO							
Test No.	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	PbO added lb./ton Ore	Copper in Soln. %	Au Extraction Oz./ton Ore	Relative Au Extraction %	Mol. Ratio NaCN/Cu	Ratio Au/NaCN
230	.025-.0180	0.70	.025-.0130	1.20	Nil	Nil	.560	77.7	---	111
231	.050-.0390	1.10	.025-.0160	0.90	Nil	Nil	.600	83.3	---	76
232	.075-.0630	1.20	.025-.0160	0.90	Nil	Nil	.710	98.6	---	82
233	.100-.0840	1.60	.025-.0165	0.85	Nil	Nil	.720	100.0	---	63
234	.025-.0030	2.20	.025-.0165	0.85	Nil	.008	.130	18.1	3.6	8.2
235	.050-.0060	4.40	.025-.0200	0.50	Nil	.014	.280	38.9	4.1	8.8
236	.075-.0120	6.30	.025-.0240	0.10	Nil	.024	.310	43.1	3.4	7.9
237	.100-.0185	8.15	.025-.0280	-0.30	Nil	.032	.340	47.3	3.3	5.8
238	.025-.0020	2.30	.025-.0175	0.75	0.50	.006	.170	23.6	5.0	10.3
239	.050-.0070	4.30	.025-.0220	0.30	0.50	.014	.380	52.8	4.0	12.3
240	.075-.0160	5.90	.025-.0240	0.10	0.50	.020	.520	72.2	3.8	12.3
241	.100-.0250	7.50	.025-.0280	-0.30	0.50	.026	.570	79.2	3.7	10.6

Tests 230-233 were carried out on the pyrite ore.
Tests 234-241 were carried out on the pyrite, copper sulphide ore.

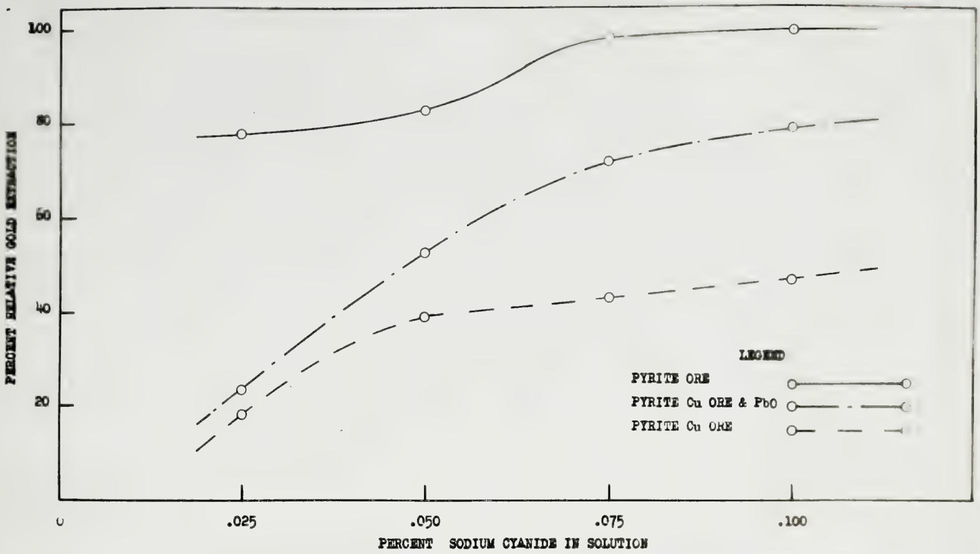

FIG. 14 EFFECT OF PbO AND VARYING SODIUM CYANIDE STRENGTH ON THE RELATIVE GOLD EXTRACTION IN THE CYANIDATION OF A PYRITE AND PYRITE COPPER SULFIDE ORE.

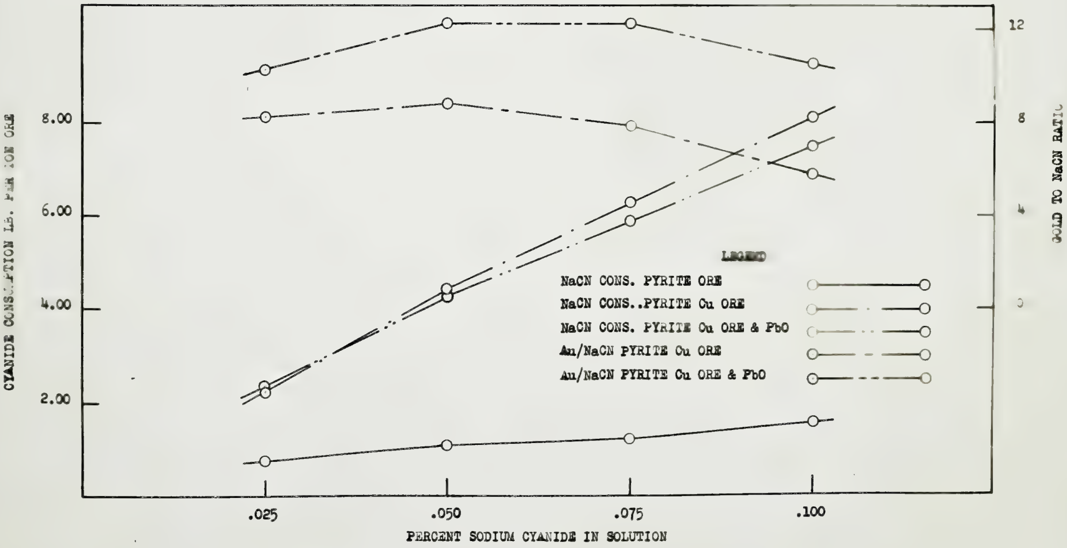

FIG. 15 EFFECT OF PbO AND VARYING SODIUM CYANIDE STRENGTH ON THE GOLD TO NaCN RATIO AND SODIUM CYANIDE CONSUMPTION IN THE CYANIDATION OF A PYRITE AND PYRITE COPPER SULPHIDE ORE.

INVESTIGATION No. 23. Combined effect of low pH and varying PbO on the solubility of copper in the cyanidation of a copper sulphide ore - Table 23.

As both a low pH and PbO additions give a reduction in copper solubility, tests were run at a pH of 7.5 with the addition of PbO varying from 0.00 to 3.00 lb. per ton ore.

Results:

Cu - solubility constant at .022%,

NaCN - consumption constant,

NaCN/Cu - constant but high,

pH - ranged from 7.5 at beginning of agitation to 7.2 at completion of agitation.

Discussion of Results:

Amphoteric substances have the property of being more soluble in an acidic or basic solution than in a neutral solution. Investigational results indicate that at a low pH of 7.5 the effect of PbO in reducing copper solubility is destroyed. A possible explanation of this phenomenum is the decrease in the solubility of PbO as a result of its amphoteric nature, thus preventing its subsequent coating of the copper minerals.

The high mol. ratio of NaCN/Cu indicates a partial titration only of the total cyanide at the low pH.

Table 23. - Combined Effect of low pH and varying PbO on the Solubility of Copper in the Cyanidation of a Copper Sulphide Ore

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	pH Range	PbO added lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
282	.100-.0360	6.40	7.5-7.2	Nil	.022	3.8
283	.100-.0345	6.55	7.5-7.2	0.10	.022	3.9
284	.100-.0340	6.60	7.5-7.2	0.30	.022	3.9
285	.100-.0350	6.50	7.5-7.2	0.50	.022	3.8
286	.100-.0350	6.50	7.5-7.2	0.70	.022	3.8
287	.100-.0350	6.50	7.5-7.2	1.00	.022	3.8
288	.100-.0330	6.70	7.5-7.2	2.00	.022	3.95
289	.100-.0410	5.90	7.5-7.2	3.00	.018	4.3

In all tests the alkalinity was provided by 20 pounds of Na_2HPO_4 and 6 pounds of H_3PO_4 per ton of solution.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

INVESTIGATION No. 24. Effect of a strong oxidizer, NaOCl (perfex) on the solubility of copper in the cyanidation of a copper sulphide ore - Table 24.

To study the effect of oxidizers as a means of controlling copper solubility, tests were run on a copper sulphide ore with the addition of increasing amounts of NaOCl. Since in the discussion on copper it appeared that the copper complex ion was formed by a mechanism similar to the following:

$$Cu^{++} + 2CN^{-} = Cu(CN)_2$$

$$2Cu(CN)_2 = 2CuCN + C_2N_2$$

$$CuCN + 2CN^{-} = Cu(CN)_3^{=}$$

it seemed probable that in an oxidizing atmosphere divalent copper would prevail, thereby, reducing the cyanide to copper ratio from 3 to 2. Also, the possible precipitation of the copper as $Cu(OH)_2$ would result in a further reduction in cyanide consumption.

Results:

Cu - Solubility decreased from .034% to 0.00%,

NaCN - consumption increased from 7.50 to 9.70 lb. per ton ore,

NaCN/Cu - increased from 2.9 to 15.8,

CaO - consumption erratic but essentially constant,

pH - slight decrease from 11.35 to 11.10,

R.P. - reducing power decreased proportionately from 84 to zero.

Discussion of Results:

Results showed that a reduction in copper solubility is affected, however, not by the mechanism proposed above. The strong oxidizing action of the NaOCl results in a decomposition of the cyanide radical into its elemental components C and N and evolving them as CO_2, CO, NO_2 and NH_3. Thus, the reduced copper solubility must be attributed to insufficient cyanide strength. Similarly the high cyanide to copper ratio is due to the abnormal cyanide destruction.

Table 24. - Effect of a Strong Oxidizer NaOCl (Perfex) on the Solubility of Copper in the Cyanidation of a Copper Sulphide Ore

	NaCN		CaO			NaOCl		Copper	Mol.
Test No.	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	pH	(Perfex) lb./ton Soln.	R.F.	in Soln. %	Ratio NaCN/Cu
330	.100-.0250	7.50	.000-.0100	-1.00	11.35	Nil	84	.034	2.9
331	.100-.0170	8.30	.000-.0110	-1.10	11.35	10	80	.032	3.4
332	.100-.0110	8.90	.000-.0115	-1.15	11.30	20	60	.026	4.4
333	.100-.0055	9.45	.000-.0115	-1.15	11.25	30	40	.018	6.3
334	.100-.0030	9.70	.000-.0100	-1.00	11.20	40	28	.008	15.8
335	.100-.0020	9.80	.000-.0110	-1.10	11.10	50	8	trace	-
336	.100-.0030	9.70	.000-.0115	-1.15	11.10	60	-	Nil	-
337	.100-.0030	9.70	.000-.0175	-1.75	11.20	80	-	Nil	-

No. CaO was added in these tests.

INVESTIGATION No. 25. Combined effect of PbO and Na_2O_2 on the solubility of copper in the cyanidation of a copper sulphide ore - Table 25.

To continue the study of oxidizers, an oxidant, Na_2O_2, with a weaker oxidation potential was employed. Tests were carried out on the copper sulphide ore with 0.50 pound PbO and 2.00 lb. PbO and varying the amounts of Na_2O_2 from 0.00 to 5.00 lb. per ton ore.

Results:

Cu - 0.50 lb. PbO - solubility constant,
2.00 lb. PbO - solubility decreased slightly from .009 to .006 per cent,
NaCN - 0.50 lb. PbO - consumption constant,
2.00 lb. PbO - consumption decreased slightly from 2.45 to 1.85 lb. per ton ore,
NaCN/Cu - essentially constant but high,
CaO - consumption increased for both series.

Discussion of results:

With 0.50 lb. of PbO, the addition of Na_2O_2 appears to have little effect on copper solubility or cyanide consumption. However, with 2.00 lb. PbO a slight decrease in both copper solubility and cyanide consumption is obtained. It is possible that in the latter instance the Na_2O_2 has oxidized the $Cu(CN)_3^{2-}$ to $Cu^{++} + 3CN^- + (-)$ to a limited extent, with its subsequent precipitation as $Cu(OH)_2$.

Table 25. - Combined Effect of PbO and Na_2O_2 on the Solubility of Copper in the Cyanidation of a Copper Sulphide Ore.

Test No.	NaCN		CaO		PbO added lb./ton Ore	Na_2O_2 added lb./ton Ore	Copper in Soln. %	Mol. Ratio NaCN/Cu
	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore				
274	.100-.0640	3.60	.025-.0280	-0.30	0.50	Nil	.014	3.3
275	.100-.0625	3.75	.029-.0345	-0.55	0.50	0.50	.015	3.25
276	.100-.0650	3.50	.033-.0360	-0.30	0.50	1.00	.013	3.5
277	.100-.0610	3.90	.061-.0585	+0.25	0.50	5.00	.014	3.6
278	.100-.0755	2.45	.025-.0310	-0.60	2.00	Nil	.009	3.5
279	.100-.0780	2.20	.029-.0325	-0.35	2.00	0.50	.008	3.6
280	.100-.0815	1.85	.033-.0340	-0.10	2.00	1.00	.006	4.0
281	.100-.0800	2.00	.061-.0560	+0.50	2.00	5.00	.007	3.7

Alkalinity due to Na_2O_2 was included in the figures given for "CaO Range % Solution."

INVESTIGATION No. 26. Effect of PbO and varying amounts of Na_2O_2 on gold extraction, copper solubility, sodium cyanide consumption and sodium hydroxide consumption in the cyanidation of a pyrite and pyrite copper sulphide ore - Table 26 - Fig. 16.

Tests were performed on a pyrite copper sulphide ore with the optimum addition of 0.50 lb. PbO per ton of ore and varying the amount of Na_2O_2 from 0.00 to 3.00 lb. per ton ore.

Results:

Au - Extraction increased to a maximum of 106.0% at 1.0 lb. Na_2O_2 and then decreased with further additions,

Cu - solubility decreased slightly from .024% to .020%,

NaCN - consumption decreased from 6.30 to 5.50 lb. per ton ore,

Au/NaCN - maximum value of 18.8 at 1.0 lb. Na_2O_2, coincident with maximum Au recovery,

NaCN/Cu - ratio constant,

NaOH - consumption increased,

R.P. - constant at 90,

pH - slight increase.

Discussion of results:

The increase in gold recovery to reach a maximum with increasing amounts of Na_2O_2 and the drop in recovery

with further additions of Na_2O_2 beyond this maximum, substantiates the proposed mechanism for the dissolution of gold by oxygen and cyanide, as outlined in the theory of cyanidation.

It has been previously proposed that copper solubility, with corresponding cyanide consumption, may be reduced by oxidation of $Cu(CN)_3^{2-}$ as follows:

$$Cu(CN)_3^{2-} = Cu^{++} + 3CN^- + (-)$$

$$Cu^{++} + 2OH^- = Cu(OH)_2 \text{ (precipitates out)}$$

The occurrence of this reaction to a limited extent may account for the slight decrease in copper solubility in this instance. The constant reducing power confirms the comparatively mild action of Na_2O_2 as an oxidant, with that of NaOCl in investigation No. 24, and suggests the use of an oxidizer with an intermediate power as a possible means of furthering the above reaction.

Table 23. - Effect of PbO and Varying Amounts of Na_2O_2 on Gold Extraction, Copper Solubility, Sodium Cyanide Consumption and Sodium Hydroxide Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	NaOH=CaO Range % Soln.	NaOH=CaO Consump. lb./ton Ore	pH	PbO added lb./ton Ore	Na_2O_2 added lb./ton Ore	R.I.	Cu in Soln. %	Mol. Ratio NaCN/Cu	Au. Extr. Oz./Ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
338	.100-.0935	0.65	.0250-.0100	0.60	11.60	Nil	Nil	14	Nil	---	.670	100.0	154
354	.100-.0570	6.30	.0250-.0280	-0.36	11.70	0.50	Nil	90	.024	3.4	.655	97.8	15.5
355	.100-.0585	6.15	.0280-.0310	-0.24	11.70	0.50	0.50	92	.022	3.6	.660	98.5	16.0
356	.100-.0435	5.65	.0322-.0310	-0.12	11.75	0.50	1.00	90	.022	3.3	.710	106.0	18.8
357	.100-.0420	5.80	.0324-.0370	0.24	11.80	0.50	2.00	88	.022	3.4	.625	93.4	16.1
358	.100-.0450	5.50	.0466-.0415	0.51	11.85	0.50	3.00	90	.020	3.7	.620	91.6	16.7

Test 338 was run as a standard test.
Alkalinity due to Na_2O_2 was included in the figures given for "CaO Range % Solution".

INVESTIGATION No. 27. Combined effect of PbO and Na_2O_2 on gold extraction, copper solubility, sodium cyanide consumption and lime consumption in the cyanidation of a pyrite and pyrite copper sulphide ore - Table 27, Fig. 17.

To determine further the relation between PbO and Na_2O_2, tests were run on a pyrite copper sulphide ore with Na_2O_2 constant and varying amounts of PbO. The optimum amount of 1.00 lb. Na_2O_2 and the less favorable addition of 5.00 lb. Na_2O_2 were employed, with PbO varying from 0.00 to 2.00 lb. per ton ore.

Results:

Au - 1.00 lb. Na_2O_2 - extraction increased to maximum of 96.6% at 1.00 lb. PbO per ton ore and then decreased to 56.0% at 2.00 lb. PbO,

5.00 lb. Na_2O_2 - maximum extraction of 78.0% at 0.30 lb. PbO and then decreased to 49.2% at 2.00 lb. PbO.

Cu - 1.00 lb. Na_2O_2 - solubility decreased from .032% to .014%,

5.00 lb. Na_2O_2 - solubility decreased from .026% to .012%,

NaCN - 1.00 lb. Na_2O_2 - consumption decreased from 7.50 lb. to 3.85 lb. per ton,

5.00 lb. Na_2O_2 - consumption decreased from 6.25 lb. to 3.80 lb. per ton,

Au/NaCN - 1.00 lb. Na_2O_2 - maximum value of 17.4 coincident with maximum gold recovery,
5.00 lb. Na_2O_2 - maximum value of 13.9 at 0.50 lb. PbO per ton ore,

NaCN/Cu - 1.00 lb. Na_2O_2 - increased from 3.1 to 3.6,
5.00 lb. Na_2O_2 - increased from 3.1 to 4.1,

CaO - 1.00 lb. Na_2O_2 - consumption increased from -0.30 to 0.42 lb. per ton ore,
5.00 lb. Na_2O_2 - consumption increased from -0.30 to 1.20 lb. per ton ore,

R.P. - 1.00 lb. Na_2O_2 - decreased from 108 to 60,
5.00 lb. Na_2O_2 - decreased from 98 to 60.

Discussion of results:

As in Investigation No. 26, the decrease in gold extraction with excess Na_2O_2 further confirms the hypothesis of an optimum oxygen concentration for each particular cyanide content, at which the cyanide and oxygen molecules appear at the gold surface in exactly the right proportion to affect a maximum rate of gold dissolution.

The respectively lower copper solubilities with the larger Na_2O_2 addition would appear to indicate the oxidation of $Cu(CN)_3^{2-}$ to $Cu^{++} + 3CN^- + (-)$ and its subsequent precipitation as $Cu(OH)_2$, or some similar mechanism.

However, the concentrations of oxygen required to affect a large reduction in copper would necessarily be in excess of those required for maximum gold dissolution and thus limit this approach as a means of further decreasing copper in solution.

The generally lower cyanide consumption with the 5.00 lb. Na_2O_2 may be attributed to the lower copper solubility. However, the higher NaCN/Cu ratio for 5.00 lb. Na_2O_2 indicates that the decrease is not sufficient to correspond with the decrease in copper and that an actual increase in cyanide consumption exists possibly due to an excess of Na_2O_2. A probable explanation is that the CN^- is oxidized to CNO^- and, as such, does not appear as free cyanide.

An examination of the reducing power values indicates that both an increase in Na_2O_2 and the decrease of copper in solution (attributed to PbO additions) results in a lowering of the reducing power of the solution.

Table 27. - Combined Effect of PbO and Na_2O_2 on Gold Extraction, Copper Solubility, Sodium Cyanide Consumption and Lime Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	PbO added lb./ton Ore	Na_2O_2 added lb./ton Ore	R.P.	Cu in Soln. %	Mol. Ratio NaCN/Cu	Au Extr. Oz./ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
309	.100-.0935	0.65	.0250-.0150	1.00	Nil	Nil	20	Nil	---	.590	100.0	154
310	.100-.0225	7.75	.0250-.0280	-0.30	Nil	Nil	112	.034	3.0	.350	59.4	7.8
311	.100-.0250	7.50	.0322-.0330	-0.08	0.30	1.00	108	.032	3.1	.440	74.6	10.0
312	.100-.0365	6.35	.0322-.0310	0.12	0.50	1.00	96	.028	3.0	.490	83.1	13.1
313	.100-.0445	5.55	.0322-.0300	0.22	1.00	1.00	88	.022	3.3	.570	96.6	17.4
314	.100-.0615	3.85	.0322-.0280	0.42	2.00	1.00	60	.014	3.6	.330	56.0	14.5
315	.100-.0375	6.25	.0610-.0520	.90	0.30	5.00	98	.026	3.1	.460	78.0	12.5
316	.100-.0450	5.50	.0610-.0515	.35	0.50	5.00	92	.020	3.6	.450	76.3	13.9
317	.100-.0490	5.10	.0610-.0510	1.00	1.00	5.00	84	.018	3.7	.375	63.6	12.5
318	.100-.0620	3.80	.0610-.0490	1.20	2.00	5.00	60	.012	4.1	.290	49.2	13.0

Test 309 was run as a standard test.
Alkalinity due to Na_2O_2 was included in the figures given for "CaO Range % Solution".

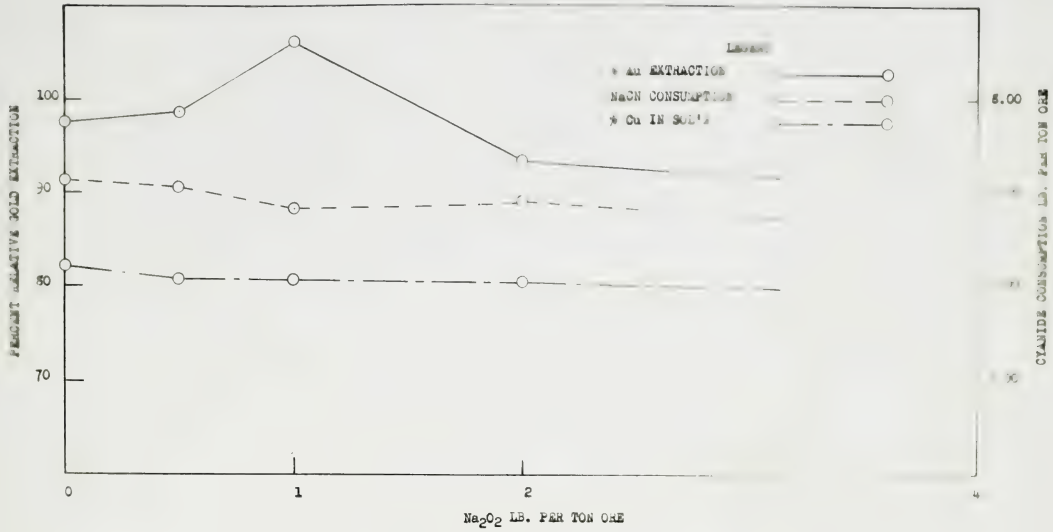

FIG. 16 EFFECT OF PbO AND VARYING AMOUNTS OF Na_2O_2 ON GOLD EXTRACTION, COPPER SOLUBILITY, AND SODIUM CYANIDE CONSUMPTION IN THE CYANIDATION OF A PYRITE COPPER SULPHIDE ORE.

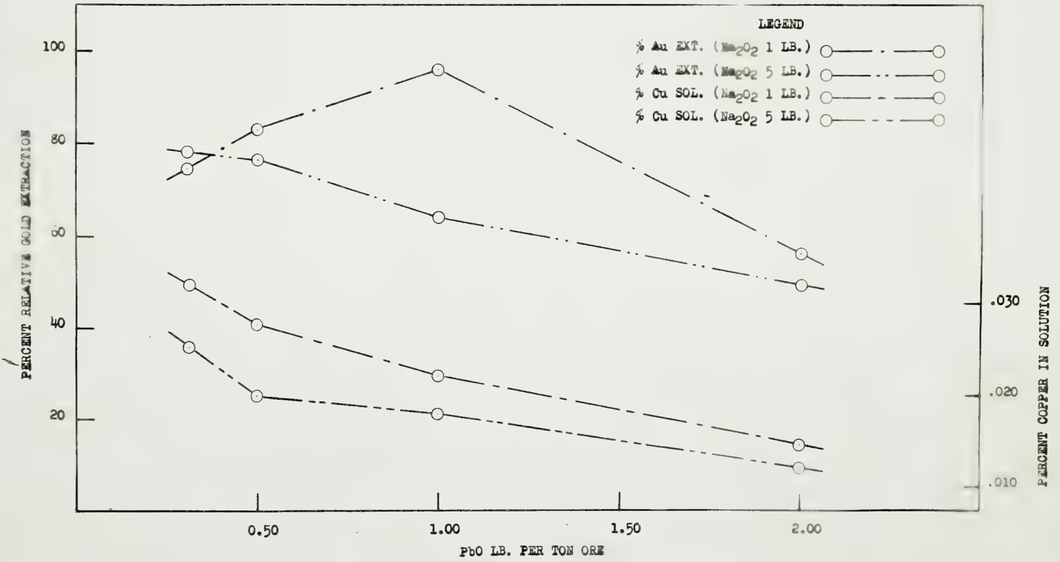

FIG. 17 COMBINED EFFECT OF PbO AND Na_2O_2 ON GOLD EXTRACTION AND COPPER SOLUBILITY IN THE CYANIDATION OF A PYRITE COPPER SULPHIDE ORE.

INVESTIGATION No. 28. Effect of phosphate, PbO and Na_2O_2 on gold extraction, copper solubility and sodium cyanide consumption in the cyanidation of a pyrite and pyrite copper sulphide ore - Table 28.

Investigation No. 12 indicated that phosphates accelerated the dissolution rate of gold as compared with the ordinary lime circuit. Tests were therefore run on a pyrite copper sulphide ore to show the effect of phosphates alone, with the optimum of 0.50 lb. PbO per ton ore and with the further optimum of 1.00 lb. Na_2O_2 per ton ore, on gold recovery in presence of copper.

Results:

Au - phosphate alone - extraction of 32.6% lower than for equivalent lime circuit,
plus PbO - slight increase to 39.3%,
plus PbO and Na_2O_2 - further increase to 43.0%,

Cu - solubility constant and high at .040%,

NaCN - slight decrease with PbO and further decrease with Na_2O_2 and PbO,

Au/NaCN - increased corresponding to Au extraction,

NaCN/Cu - essentially constant but low,

R.P. - slight increase for PbO which decreased again with Na_2O_2,

pH - lower than corresponding CaO or NaOH circuit.

Discussion of results:

The decrease in gold extraction in a phosphate circuit, as compared with the ordinary lime circuit, is apparently due to the increase in the dissolution rate of copper. This becomes apparent from an examination of the two tests. No. 327 -- Au extraction 32.6%, Copper .040% - phosphate circuit. No. 144--Au extraction 50.8%, copper 0.32% - lime circuit. The increase in the copper solubility results in a decrease in the cyanide strength and with the further inhibiting action on the gold surface by the increased copper complex ion concentration, effects a lower gold extraction. Moreover, the results indicate that in a phosphate circuit, PbO is not as effective as in a corresponding lime or sodium hydroxide cyanide circuit, possibly, due to the comparatively lower pH of the phosphate buffered solution.

Table 28. - Effect of Phosphate, PbO and Na_2O_2 on Gold Extraction, Copper Solubility and Sodium Cyanide Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore.

Test No.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	Na_2HPO_4 lb./ton Soln.	pH	PbO added lb/ton Ore	Na_2O_2 added lb./ton Ore	R.P.	Cu in Soln. %	Mol. Ratio NaCN/Cu	Au Extr. Oz./ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
326	.100-.0950	0.50	--	11.40	Nil	Nil	20	Nil	---	.675	100.0	200
327	.100-.0140	8.60	20	10.25	Nil	Nil	100	.040	2.8	.220	32.6	3.3
328	.100-.0145	8.55	20	10.25	1.00	Nil	100	.040	2.8	.225	33.3	4.0
329	.100-.0155	8.45	20	10.50	1.00	1.00	100	.040	2.7	.290	43.0	5.1

Test 326 was run in a lime cyanide solution as a standard test.
CaO range 0.025-0.0155 per cent, CaO consumption 0.95 pounds per ton of ore.

INVESTIGATION No. 29. Effect of PbO and Na_2O_2 on gold extraction, copper solubility and cyanide consumption in a lime and sodium hydroxide circuit, in the cyanidation of a pyrite and pyrite copper sulphide ore for 24 hours - Tables 29A, 29B and 29C.

To determine whether the optimum PbO and Na_2O_2 conditions as determined in previous test work, applied for a prolonged period of agitation, tests were carried out on a pyrite copper sulphide ore in both a lime and sodium hydroxide circuit. The pyrite concentrate used in these tests was ground to 87% minus 200 mesh.

Results:

Au -	Relative Extraction %		
	CaO	.025% NaOH	.050% NaOH
pyrite ore	100.0	107.0	----
pyrite Cu ore	95.9	102.9	----
pyrite Cu ore + PbO	115.3	109.8	112.5
pyrite Cu ore + PbO + Na_2O_2	122.2	101.4	107.0

Cu - solubility increased with time but at a gradual creased rate to reach a maximum of 0.128% copper i.e. the total copper content of the ore was soluble in 24 hours,

NaCN - increased consumption with time, greater consumption with PbO which is reduced slightly by Na_2O_2,

Au/NaCN - increased with addition of PbO and Na_2O_2,

NaCN/Cu - decreased with time,

pH - higher for pyrite copper ore than pyrite ore,

R.P. increased for copper,

increased slightly by PbO,

decreased slightly by Na_2O_2

Discussion of results:

The investigational results follow the general trends established in previous test work. However, the maintaining of cyanide strength throughout the tests and the inability to establish the actual time the recoveries are effected, tends to screen the full effects of PbO and Na_2O_2 in decreasing copper solubility and improving gold extraction.

An exception to the general trends established previously is the decreased gold recovery with the addition of Na_2O_2 when operating in a NaOH circuit. The importance of alkalinity control in conjunction with PbO is illustrated by the increase in gold extraction for an alkalinity of .050% NaOH as compared to .025% NaOH.

The gradual decrease in the NaCN/Cu ratio to values below 3, with increasing copper solubilities, infers the formation of copper complexes other than $Cu(CN)_3^{2-}$. The higher pH for solutions containing copper is attributed to the formation of OH^- ions by the dissolution of copper.

Table 29 A. - Effect of PbO and Na_2O_2 on Gold Extraction, Copper Solubility, Cyanide Consumption and Lime Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore for 24 hours.

Test No.	Time Accum.	NaCN Range % Soln.	NaCN Consump. lb./ton Ore	CaO Range % Soln.	CaO Consump. lb./ton Ore	pH	PbO added lb./ton Ore	Cu in Soln. %	Mol. Ratio NaCN/Cu	R.P.	Au Extr. Oz./ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
381	2:00	.100-.0765	2.35										
	12:00	.100-.1000	Nil										
	24:00	.100-.1000	Nil	.025-.0090	1.60	11.35	Nil	Nil	---	64	.720	100.0	43
			2.35										
282	2:00	.100-.0150	8.50					.026	4.2				
	4:00	.100-.0450	5.50					.044	4.1				
	6:00	.100-.0620	3.30					.060	3.9				
	12:00	.100-.0530	4.70					.080	3.7				
	24:00	.100-.0630	3.70	.025-.0315	-0.65	11.35	Nil	.128	2.7	705	.690	95.8	3.7
			26.20										
383	2:00	.100-.0085	9.15					.024	4.9				
	4:00	.100-.0405	5.35					.052	3.8				
	6:00	.100-.0540	4.90					.064	4.0				
	12:00	.100-.0480	5.20					.096	3.4				
	24:00	.100-.0660	3.40	.025-.0325	-0.75	11.35	0.50	.128	2.9	610	.830	115.3	4.1
			28.30										
384	2:00	.100-.0190	8.10					.026	4.0				
	4:00	.100-.0425	5.75					.060	3.0				
	6:00	.100-.0535	4.35					.064	3.8				
	12:00	.100-.0465	5.35					.096	3.2				
	24:00	.100-.0680	3.20	.0322-.0330	-0.10	11.80	0.50	.128	2.7	700	.880	122.2	4.5
			27.05										

Test No. 381 was run on the pyrite ore.
Test Nos. 382 to 384 were run on the pyrite copper sulphide ore.
1 lb. of Na_2O_2 per ton ore was added to test No. 384.

Table 29 B. - Effect of PbO and Na_2O_2 on Gold Extraction, Copper Solubility, Cyanide Consumption and Sodium Hydroxide Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ore for 24 hours.

		NaCN		NaOH = CaO									
Test No.	Time Accum.	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	pH	PbO added lb./ton Ore	Cu in Soln.	Mol. Ratio NaCN/Cu	M.P.	Au Extr. Oz./ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
385	2:00	.100-.0730	2.20										
	12:00	.100-.0995	.05										
	24:00	.100-.1000	Nil	.025-.009	1.60	11.30	Nil	Nil	---	72	.770	107.0	48
			2.25										
386	2:00	.100-.0205	7.95					.028	3.7				
	4:00	.100-.0490	5.10					.052	3.5				
	6:00	.100-.0560	4.40					.060	3.8				
	12:00	.100-.0600	4.00					.104	2.7				
	24:00	.100-.0670	3.30	.025-.034	-0.90	11.75	Nil	.128	2.6	630	.740	102.8	4.2
			24.75										
387	2:00	.100-.0160	8.40					.026	4.2				
	4:00	.100-.0450	5.50					.056	3.2				
	6:00	.100-.0560	4.40					.064	3.7				
	12:00	.100-.0575	4.25					.104	2.8				
	24:00	.100-.0660	3.40	.025-.036	-1.10	11.80	0.50	.128	2.6	690	.790	109.7	[illegible]
			25.95										
388	2:00	.100-.0170	8.30					.026	4.1				
	4:00	.100-.0460	5.40					.052	3.4				
	6:00	.100-.0580	4.20					.060	3.9				
	12:00	.100-.0595	4.05					.104	2.7				
	24:00	.100-.0655	3.45	.032-.039	-0.70	11.80	0.50	.128	2.6	680	.730	101.4	4.0
			25.40										

Test 385 was run on the pyrite ore.
Test 386-388 were run on the pyrite copper sulphide ore.
1 lb. of Na_2O_2 per ton ore was added to test No. 388.

Table 29 C. - Effect of PbO and Na O on Gold Extraction, Copper Solubility, Cyanide Consumption and Sodium Hydroxide Consumption in the Cyanidation of a Pyrite Copper Sulphide Ore for 24 hours.

Test No.	Time Accum.	Range % Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	pH	PbO added lb./ton Ore	Cu in Soln. %	Mol. Ratio NaCN/Cu	R.P.	Au Extr. Oz./ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
389	2:00	.100-.0210	7.90					.026	3.9				
	4:00	.100-.0410	5.90					.052	3.4				
	6:00	.100-.0545	4.55					.072	3.3				
	12:00	.100-.0560	4.40					.104	2.8				
	24:00	.100-.0655	3.45	.050-.052	-0.20	11.90	0.50	.122	2.7	700	.810	112.5	1.7
			26.20										
390	2:00	.100-.0225	7.75					.028	3.6				
	4:00	.100-.0455	5.45					.056	3.1				
	6:00	.100-.0570	4.30					.068	3.3				
	12:00	.100-.0550	4.50					.104	2.8				
	24:00	.100-.0675	3.25	.057-.055	0.20	11.90	0.50	.120	2.6	700	.770	107.0	1.8
			25.25										

Tests 389 and 390 were run on a pyrite copper sulphide ore.
1 lb. Na_2O_2 per ton ore was added to test 390.

INVESTIGATION No. 30. Effect of PbO, in ores of different copper contents, on gold extraction, copper solubility, cyanide consumption, and sodium hydroxide consumption in the cyanidation of pyrite and pyrite copper sulphide ore - Table 30 - Fig. 18.

To determine if the relationships established in the preceding investigations held true for ores containing different percentages of copper, tests were conducted on three ores which contained 0.67%, 1.34% and 2.01% Cu. The percentage of copper mineral was the only variable.

Results:

Au - 0.67% Cu - extraction increased to a maximum of 83.6% at 0.50 lbs. PbO, and decreased when more PbO added.

1.34% Cu - extraction increased to a maximum of 81.5% at 0.50 lbs. PbO, and then decreased.

2.01% Cu - extraction increased to a maximum of 66.5% at 1.0 lb. PbO, and then decreased.

Cu - 0.67% Cu - Solubility decreased from 0.032% to 0.014% Cu,

1.34% Cu - Solubility decreased from 0.044% to 0.026% Cu,

2.01% Cu - solubility decreased from 0.052% to 0.034% Cu,

NaCN - 0.67% Cu - consumption decreased from 7.70 to 4.25 lb. per ton ore,

1.34% Cu - consumption decreased from 8.90 to 6.65 lb. per ton ore,

2.01% Cu - consumption decreased from 9.15 to 8.20 lb. per ton ore,

Au/CN - 0.67% Cu - ratio increased erratically from 13.5 to 17.3,

1.34% Cu - ratio showed no significant change - average value was 9.6,

2.01% Cu - ratio showed no significant change - average value was 6.9,

NaCN/Cu - 0.67% Cu - ratio increased from 3.1 to 3.9,

1.34% Cu - ratio increased from 2.6 to 3.3,

2.01% Cu - ratio increased from 2.3 to 3.1,

CaO - There was a small increase (negative to less negative) in each case,

pH - remained constant at value of 11.75,

R.P. - 0.67% Cu - values decreased from 100 to 60,

1.34% Cu - values increased from 100 to 118 at 1.00 lb. PbO and then decreased to 92,

2.01% Cu - values increased from 86 to 128 at 1.00 lb. PbO and then decreased to 114.

Discussion of Results:

The decreased gold extraction, the increased copper

solubility, and the increased cyanide consumption can all be attributed to the increase in copper content of the ore.

The optimum gold extractions for the three percentages of copper are obtained at approximately the same litharge addition. This suggests that the action of lead in inhibiting the copper minerals from the action of cyanide is one of adsorption. In adsorption of this type the consumption of the adsorbed phase by the adsorbent is small. By increasing the amount of the adsorbent, the increased consumption of the adsorbed phase is small. In this particular case with the copper minerals as the adsorbent and the lead as the adsorbed phase, the consumption of lead with increased copper minerals would not be significant.

The low values (average 2.6) of the cyanide copper ratio for 2.01% Cu ore indicate that the copper may be going into solution in some other manner than by the formation of $Cu(CN)_3^{=}$.

Table 30. - Effect of PbO, in Ores of Different Copper Contents, on Gold Extraction, Copper Solubility, Sodium Cyanide Consumption, and Sodium Hydroxide Consumption in the Cyanidation of a Pyrite and Pyrite Copper Sulphide Ores.

	NaCN		NaOH = CaO									
Test No.	Range %Soln.	Consump. lb./ton Ore	Range % Soln.	Consump. lb./ton Ore	pH	PbO added lb./Ton Ore	R.T.	Cu in Soln. %	Mol. Ratio NaCN/Cu	Au Extr. Oz./ton Ore	Rel. Au Extr. %	Ratio Au/NaCN
359	.100-.0910	0.90	.025-.0170	0.80	11.60	Nil	16	Nil		.700	100.0	
360	.100-.0230	7.70	.025-.0275	-0.25	11.75	Nil	100	.032	3.1	.320	45.7	5.9
361	.100-.0380	6.20	.025-.0270	-0.20	11.70	0.50	92	.032	2.5	.585	83.6	13.5
362	.100-.0470	5.30	.025-.0265	-0.15	11.70	1.00	82	.022	3.1	.575	82.2	15.5
363	.100-.0515	4.85	.025-.0255	-0.05	11.75	1.50	66	.016	3.6	.480	68.7	14.1
364	.100-.0575	4.25	.025-.0245	0.05	11.70	2.00	60	.014	3.9	.515	73.6	17.3
365	.100-.0110	8.90	.025-.0295	-0.45	11.75	Nil	100	.044	2.6	.170	24.3	2.7
366	.100-.0160	8.40	.025-.0300	-0.50	11.75	0.50	110	.036	3.0	.570	81.5	9.7
367	.100-.0210	7.90	.025-.0290	-0.40	11.75	1.00	118	.026	3.9	.520	74.3	9.4
368	.100-.0270	7.30	.025-.0280	-0.30	11.75	1.50	102	.030	3.2	.500	71.5	9.8
369	.100-.0335	6.65	.025-.0275	-0.25	11.75	2.00	92	.028	3.5	.445	63.6	9.6
370	.100-.0085	9.15	.025-.0295	-0.45	11.75	Nil	86	.052	2.3	.155	22.2	2.4
371	.100-.0105	8.95	.025-.0305	-0.55	11.75	0.50	108	.046	2.4	.400	57.2	6.4
372	.100-.0125	8.75	.025-.0295	-0.45	11.75	1.00	120	.044	2.6	.465	66.5	7.6
373	.100-.0140	8.60	.025-.0290	-0.40	11.80	1.50	116	.044	2.5	.400	57.2	6.7
374	.100-.0180	8.20	.025-.0285	-0.35	11.80	2.00	114	.034	3.1	.385	55.5	6.8

Test 359 was run in a lime cyanide solution as a standard test.
Test 360-364 - 0.67% copper added (standard)
365-369 1.34 " "
370-374 2.01 " "

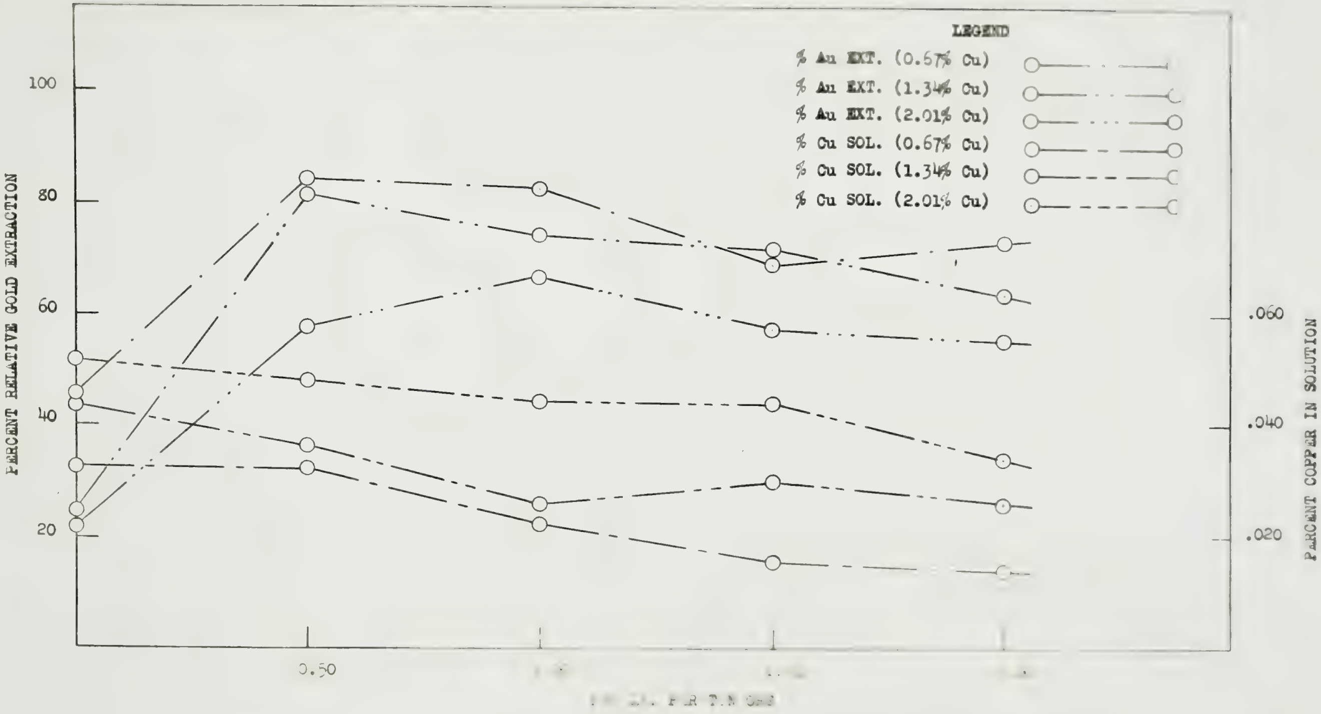

FIG. 18 EFFECT OF PbO, IN AN ORE OF VARIABLE COPPER CONTENT [illegible]
SOLUBILITY IN THE CYANIDATION OF A PY[illegible]

DISCUSSION

SUMMARY and CONCLUSIONS

RECOMMENDATIONS

DISCUSSION, SUMMARY AND CONCLUSIONS, AND RECOMMENDATIONS

I DISCUSSION OF INVESTIGATIONAL RESULTS

Investigational results substantiate the postulation that the underlying factor in the cyanidation of cupriferous gold ores is the establishment of a differential dissolution rate for copper and gold. This differential is attained in varying degrees, by the application of reagent control and chemical principles, which are, in order of their effectiveness, mineral coating, pH and alkalinity, oxidation, cyanide concentration, and precipitation.

Mineral coating - The application of the mineral coating mechanism gives both favorable and unfavorable dissolution differentials depending on the type of substance employed to coat the mineral. Lead, in small amounts, is found to coat the copper minerals more effectively than gold when tests are run on individual copper ores (with no gold present) and gold ores (with no copper present). By increasing the amounts of lead the preferential coating ability of lead is decreased until a point is reached when lead coats the gold to the same extent as copper (investigation No. 14 and testsNos. 140 to 143 investigation No. 17).

However when copper and gold are combined the attainment of a differential is more complex than by lead coating alone. When gold is cyanided in the presence of copper, the gold recovery is reduced, which has been considered presumbably due to cyanide depletion according to past investigators. But there are strong indications that the copper complex ion,

formed by copper dissolution, coats the gold surface preventing its dissolution by cyanide. Lead appears to have a dual role with respect to copper; first, that of decreasing the copper solubility by adsorption of the lead on the copper minerals forming an insoluble coating and , second, that of preventing the copper ions from coating the gold, which is presumably caused by copper ions adsorbing on, or reacting with the lead. Thus when increasing amounts of lead are added there is first an increased recovery of gold attributed to the decreased copper solubility and the repression of the copper ions coating the gold. With further additions of lead the gold recovery decreases because the coating of the gold by lead becomes prominent and overrides the beneficial effects of copper suppression by the lead.

The foregoing reasoning is borne out by the following experimental evidence. In the cyanidation of gold pyrite ore, test No. 230, investigation No. 22, a gold recovery of 77.7 per cent was obtained with a cyanide strength ranging between 0.025 - 0.018 per cent. But, in the cyanidation of a gold copper ore, test No. 237 investigation No. 22, a gold recovery of only 47.3 per cent was obtained with a cyanide strength ranging between 0.100 - 0.018 per cent. Indications are that copper is affecting gold dissolution. This is further brought out when tests 144 and 146, investigation No. 17, are compared. The cyanide strength for test 146, is lowered to a greater degree than for test 144, but the gold recovery for test 146 was higher than for 144. It is clear then, that cyanide

depletion is not the only factor affecting the gold dissolution. Test 146 differs from test 144 in that o.3 lb. PbO per ton ore is added to test 146. This suggests that PbO has prevented the copper from coating the gold in some manner. The following mechanisms are advanced to explain the above results:

(1) Pb ions adsorb on gold,

(2) Pb ions adsorb on copper minerals,

These two functions account for the decrease in the solubility of gold and copper.

(3) Copper ions adsorb on gold,

This indicates why the dissolution of gold in the presence of copper ions is hindered to a greater degree than could be predicted from cyanide depletion alone.

(4) Copper ions adsorb on or react with PbO or Pb ions,

This illustrates how litharge decreases the effect of (3), that is, when lead is added the copper ions now adsorb on or react with the lead in preference to adsorbing on the gold. The maximum gold extraction is obtained by the correct balance of all mechanisms. Too little PbO does not fully utilize the advantages of (2) and (4), while too much lead by (1) nullifies the action of (2) and (4). This is nicely shown by Table 17 and Fig. 9, when an increase of PbO up to 0.50 lb. per ton ore gives the maximum extraction, while a further litharge increase reduces the extraction.

The actual form that the lead is in, to be effective, seems to be as an ion or as lead hydroxide and not as the insoluble lead compound. This is shown by the results of investigations Nos. 15, 14 and 16 in which a soluble, partially soluble and insoluble lead compound is employed.

The effectiveness of lead is subject to the degree and type of alkalinity of the solution. Because amphoteric substances are more soluble in strong bases (or strong acids) and as PbO has amphoteric properties it is more efficient in solutions of high pH, that is, it is dependent on the degree of alkalinity. That the type of alkali employed to give the required pH further influences the action of litharge is indicated by investigation No. 19. Here, although PbO in a sodium hydroxide circuit does not coat the copper and gold to the same extent as in a lime circuit, differential established in the sodium hydroxide circuit is the better.

Like litharge, amines effectively decreased the copper solubility, but unlike litharge the amines, even in small amounts, greatly decreased gold dissolution. That only small amounts of amines are required to greatly lower copper solubility is attributed to a surface coating, impervious to cyanide solutions, rather than precipitation en masse. The surface coating may be obtained either by the formation of a copper amino precipitate or by the adsorption of the amine on the mineral surface.

While the use of amines in the experimental work did not give a favorable differential of gold to copper dissolution, the results are nevertheless significant. If the principle of surface coating by organic compounds could be extended to selective adsorption in the right direction, it would be a powerful weapon in combating the detrimental effects of copper and similar cyanicides in the cyanidation of gold ores.

pH and Alkalinity - The study of pH and HCN dissociation indicates that a decrease in pH is comparative to a decrease in the free cyanide strength of the solution. Investigational work shows that a decrease in both gold and copper dissolution may be effected by a lowering of pH. A comparison of the two dissolution curves with pH (Figs. 6 and 7) indicates a close similarity in their slopes and as such limits pH control as a means of establishing a differential dissolution rate between copper and gold. With copper the decreased rate is not coincident with the theoretical HCN dissociation curve, possibly due to the reduced cyanide strength as a result of cyanide consumption by copper. That the decreased rate for gold is not coincident with the theoretical curve may be attributed to the far from proportionate dissolution rate of gold with cyanide concentration.

The apparent high cyanide consumption (investigations No. 10, 11, 12 and 23) at low pH is misleading, in that

only a partial titration of the total cyanide is obtained because of incomplete dissociation. The remainder appears as consumed cyanide.

The type of alkalinity is a factor in the dissolution of gold and copper. A comparison of investigations No. 17 and 19 for the dissolution of gold alone substantiates the work of other investigators as to the inhibiting action of Ca^{++} when introduced by CaO. Investigation No. 2 shows that this inhibiting nature is not extended to copper. While NaOH essentially had no effect on the dissolution rate of copper, the addition of phosphates (test No. 298, Table 10) accelerates its dissolution rate. Phosphates similarily appear to improve the dissolution of gold (test No. 230, Table 12) as compared to a lime circuit, but it is probable that this improvement should be considered a lack of inhibiting action, rather than an accelerating action due to phosphates.

Oxidizers and Oxidation - The prevention of complex copper cyanide ion formation by oxidation seems to be borne out by investigations No. 26, 27 and 28. With all other factors constant, increased amounts of sodium hydroxide decreases the copper solubility. The hydroxyl radical, however, is too weak an oxidizing agent to effect the lowering of copper (investigation No. 2 and 3). Perfex (NaOCl) likely would decrease the copper in solution by oxidation, but being too strong it destroys the dissolving agent, namely, the cyanide. An additional feature of the

oxidizers is noted from investigations No. 2,3,21,26 and 27. In these instances, the cyanide consumption increases, and the increase is attributed to oxidation of the cyanide ion to the cyanate ion. Results from investigation No. 28 appear to discredit this supposition as the cyanide consumption decreases with the addition of sodium peroxide. But in this investigation only 1 lb. Na_2O_2 per ton ore is used while in other investigations, in particular No. 27, the increase is noted when 5 lb. Na_2O_2 per ton ore is employed. It is believed that there are two opposing tendencies: first, the oxidation of potential cyanicides to non-cyanicides resulting in a cyanide saving; second, the oxidation of cyanide to cyanate. The first condition predominates at a certain degree of oxidation while the second predominates at a higher degree of oxidation.

Investigation No. 26 tends to confirm the heterogeneous reaction hypothesis. Here increased amounts of peroxide gives an optimum gold recovery at 1.0 lb. Na_2O_2 per ton ore. Further additions of peroxide decreases the gold extraction, substantiating the idea that oxygen and cyanide must be in the correct proportions to give an optimum gold dissolution.

Cyanide Concentration - Investigations confirm the prediction that an optimum differential exists at a low cyanide strength, when operating conditions are such that the oxygen content remains constant. Investigations

Nos. 6 and 22 when cyaniding copper ore alone and gold ore alone respectively, shows the differential to be at 0.025% NaCN. When the two ores are combined the optimum differential is shifted to 0.050% NaCN. There are two possible explanations for this optimum differential shift; either the copper dissolution effectively lowers the cyanide strength to where the original optimum differential exists (at 0,025% NaCN) or the adsorption of copper on the gold shifts the location of the best fifferential by reducing the gold dissolution rate.

Precipitation - Additions of either xanthate or stearic acid do not appear to form an insoluble compound more stable than $Cu(CN)_3^{2-}$. While the addition of amines did effect a reduction in copper solubility, as previously discussed, it is attributed to a surface coating, impervious to cyanide solutions, rather than precipitation en masse.

Copper Complex Formation - The experimental work indicates that $Cu(CN)_3^{2-}$ is not as prevalent as is suggested by theoretical considerations or the opinions of other investigators. Results of the present investigation show that of all the tests carried out, although the cyanide consumption to copper dissolution ratio of 3 predominated, a small percentage has a higher ratio and a small percentage (13% of the investigations performed) has a lower ratio.

While the higher ratios suggest the formation of complexes with a higher cyanide to copper ratio, this is on the assumption that the total cyanide consumption is due to copper dissolution. Aportion of this cyanide consumption, however, may be attributed to the presence of pyrite and addition reagents and thus does not necessarily mean that a higher complex is formed.

Of the lower ratios the greater portion occur when the copper in solution is above 0.034%. This indicates that high copper may favor the formation of a copper complex with a lower cyanide to copper ratio. Conditions under which the tests were performed are such, that, copper solubilities beyond 0.034% result in a low free cyanide content. This may be another factor affecting the formation of complexes with a lower cyanide to copper ratio.

While from the theoretical discussion on the dissolution of copper, indications are that the formation of $Cu(CN)_3^{2-}$ is favored and that abnormal concentrations of Cu and CN are required for the formation of lower ratio complexes, this is on the assumption that the reaction is homogeneous. However, if the dissolution of copper is considered a heterogeneous reaction, the low cyanide concentration would necessarily result in a low diffusion rate of the CN^- to the surface of the copper

minerals. As such it is possible that the formation of a copper complex with a lower cyanide to copper ratio takes place, when the conditions outlined prevail.

II SUMMARY AND CONCLUSIONS

1. The detrimental effect of copper in the cyanidation of cupriferous gold ores is attributed not only to cyanide depletion, but also to the coating of the gold by copper ions. The cyanide consuming copper complex is most probably $Cu(CN)_3^{=}$, but conditions may be such that higher or lower complex ions are formed.

2. Previous experimental work and results from this investigation indicate the dissolution of gold in cyanide solutions is a heterogeneous reaction, in which a maximum gold dissolution is dependent on the maintenance of a definite ratio of cyanide to oxygen.

3. In the cyanidation of a cupriferous gold ore correct additions of litharge, either in a lime circuit or in a sodium hydroxide circuit, with or without an artificial oxidizer, appreciably increase the gold extraction and lower the cyanide consumption. Average comparative results are given in the following table.

Type of Ore	Type of Alkal'y.	Addition Reagents lb/T.Ore	Relative % Au Ext.	CN Cons. lb/T.Ore
Au(pyrite)	CaO	Nil	100.0	1.30
Au(pyrite)& Cu Sulphides	CaO	Nil	51.8	7.90
do	CaO	PbO-0.50	83.4	7.15
do	NaOH	PbO-0.50	92.6	6.20
do	NaOH	PbO-0.50 & Na_2O_2-1.00	101.3	5.60

! Values relative to extraction of straight cyanidation in a lime circuit on a pyrite ore.

Note: The tabled values are applicable only to the cupriferous gold ore employed in this investigation and do not necessarily apply to all cupriferous gold ores.

4. With variations of copper content of the ore from 0.67% to 2.01%, the optimum effect of PbO on gold recovery was attained by additions of PbO of 0.50 to 1.00 lb. per ton ore. Investigation results and theoretical considerations point to the fact that the range in amount of PbO additions, in which optimum results of gold recovery can be obtained, will never be large, irrespective of the percent copper in the ore, and will in all likelihood be of the order indicated above. If this conclusion is valid, then the practical mill operator will be relieved of the necessity of regulating the litharge addition to correspond with inherent fluctuations in the copper content of the ore.

5. Optimum conditions for reducing the detrimental effect of copper are subject to close control of operating conditions. Excess amounts of litharge and oxidizer reduce extraction and increase cyanide consumption. The type of oxidizing agent is important, too weak an oxidizer is ineffective, too strong an oxidizer decreases extraction and increases cyanide consumption. Both lime and sodium hydroxide, when used in their optimum ranges, are satisfactory but the latter is definitely preferable.

6. In the cyanidation of a cupriferous gold ore, in which the oxygen content is fixed by atmospheric conditions, there is a definite cyanide strength at which the detrimental effects of copper are at a minima. For the ore used in this investigation the best cyanide strength is found to be 0.050% NaCN.

7. Variation of pH alone does not offer an effective remedy. Investigational work confirms the theory that HCN exists in a partially dissociated state dependent upon pH. Therefore, the titration values of "free cyanide" are erroneous at low pH.

8. Investigations, in which amines were added, showed that these addition reagents are powerful inhibitors of copper minerals to the action of cyanide. But this action is extended to gold and is in no way selective in its inhibiting ability.

9. Addition of xanthates, stearic acid and aluminum oxide fails to improve gold extraction or decrease cyanide consumption in the cyanidation of cupriferous gold ores.

III RECOMMENDATIONS

1. When cyanidation is conducted in a controlled sodium hydroxide cyanide circuit, increased gold recovery and decreased cyanide consumption may be obtained by correct additions of litharge and sodium peroxide. The quantities of addition reagents, alkalinity strength, and cyanide concentration must be determined for each individual ore.

2. The general trend of results from the preceding investigations indicates strongly that the gold cyanide solubility reaction is of the heterogeneous type. Therefore, the most profitable future research should be an investigation to substantiate this hypothesis.

3. Further investigational work is indicated to determine the effect of variables, such as fineness of grind and type of existing copper minerals, on the optimum effectiveness of litharge.

4. The success of litharge in these investigations and preliminary experiments on lead acetate suggest that further test work be conducted to determine if other lead compounds are more efficient than litharge.

5. As the intensity of oxidation is a factor in effecting copper solubility and gold dissolution, in the cyanidation of cupriferous gold ores, it is recommended that oxidizing agents other than sodium

peroxide and sodium hypochlorite be studied.

6. Although the organic compounds used in this investigation were not effective in reducing copper solubility while maintaining maximum gold dissolution, it is thought that other organic substances may be applicable.

7. The principles of electrochemistry appear to offer a means of determining and influencing reactions in cyanide solutions. Future research is suggested in this field to establish a reliable electrochemical series of minerals likely to occur in ores that are subject to cyanidation.

8. Experimental work, other than that in this investigation has implied that catalysts (such as powdered carboniferous materials, iron, and alkali carbonates) have their application in cyanidation. It is recommended that additional research be performed along these lines with particular emphasis on the cupriferous gold ores to determine a catalyst which accelerates the gold dissolution or retards the copper solubility, or both.

9. Since arsenic and antimony are usually classed with copper as cyanicides, and are often found associated with gold, it is proposed that the application of the results of this investigation might be a successful solution to this problem.

APPENDICES

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REFERENCES

APPENDICES

APPENDIX (A)

A. Sample calculation for determining Ksp from the solubility of a compound.

Solubility of Copper Carbonate = 0.3 gms./L

Molecular weight of $CuCO_3$ = 123.6

Mol. solubility of $CuCO_3$ = 2.4×10^{-3} gm. mol./L

$CuCO_3 = Cu^{++} + CO_3^{=}$

2.4×10^{-3} gm. mol./L of $CuCO_3$ will produce

2.4×10^{-3} gm.-ion/L of Cu^{++} and

2.4×10^{-3} gm.-ion/L of $CO_3^{=}$

$$\begin{aligned} Ksp &= C_{Cu^{++}} \times C_{CO_3^{=}} \\ &= 2.4 \times 10^{-3} \times 2.4 \times 10^{-3} \\ &= 5.8 \times 10^{-6} \end{aligned}$$

B. Sample Calculation for determining mol concentration of anion required to precipitate copper from a solution of 0.100% NaCN and 0.036% Cu.

% Cu = 0.036% = 0.36 gm./L

$= \frac{0.36}{63.6} = 0.0057$ gm. mol/L

Consider all Cu as $Cu(CN)_3^{=}$

Then the amount of cyanide tied up with copper

$= 3 \times 0.0057 = 0.017$ gm. mol/L

Then the free cyanide available

= 0.021 (Gm.Mol/L for 0.100% NaCN) - 0.017

= 0.004 gm.mol/L

$Cu(CN)_3^{=} = Cu^{+} + 3CN^{-}$ Kinstab. = 5.0×10^{-28}

$$\frac{(Cu^{+})\ (CN^{-})^3}{Cu(CN)_3^{=}} = 5.0 \times 10^{-28}$$

$$\frac{(Cu^{+})(0.004)^3}{(0.0057)} = 5.0 \times 10^{-28}$$

$$(Cu^{+}) = 4.5 \times 10^{-23}$$

To determine the CNS⁻ concentration to Precipitate CuCNS

$CuCNS = Cu^{+} + CNS^{-}$ Ksp = 1.7×10^{-11}

$(Cu^{+})(CNS^{-}) = 1.7 \times 10^{-11}$

$(4.5 \times 10^{-23})(CNS^{-}) = 1.7 \times 10^{-11}$

$(CNS^{-}) = \dfrac{1.7 \times 10^{-11}}{4.5 \times 10^{-23}} = 3.8 \times 10^{11}$ gm.mol/L

C. To determine the ion concentration to form a complex ion other than $Cu(CN)_3^{=}$

$(Cu^{+}) = 4.5 \times 10^{-23}$

$\dfrac{(Cu^{+})(I^{-})^2}{(CuI_2^{-})} = 1.4 \times 10^{-9}$ = K instab. of CuI_2^{-}

with copper content of 0.0057M then (CuI_2^{-}) would be nearly 0.0057M

$$(I^{-})^2 = \frac{1.4 \times 10^{-9}}{4.5 \times 10^{-23}} \times 5.7 \times 10^{-3}$$

$(I^{-}) = 4.2 \times 10^{5}$ = ion concentration required to form form CuI_2^{-} in preference to $Cu(CN)_3^{=}$

APPENDIX (B)

Determination of mineral content by chemical analysis, decantation and mineral count.

1. Chemical analysis of the ore is made to determine the percentages of the metallic minerals.
2. A 150 gram sample of the ore is sized by decantation into eight fractions.
3. Polished sections of each fraction are prepared and a mineral count is conducted on each polished section to determine the relative abundance of the pertinent minerals. For ease of determination an arbitrary number of 20 is allotted to each particle and the relative abundance is estimated with the number 20 as the whole.
4. Chemical analysis are performed on each sized fraction.

Sample computation:

Mineral Count Cut No. 6.

	Bornite	Chalcopyrite	Covellite	Chalcocite	Pyrite
	15	5	--	--	--
	--	20	--	--	--
	10	5	1	1	3
	--	--	--	--	--
Total	2582	2404	84	40	250
Percent	48.2	44.9	1.5	0.7	4.7

From the relative abundance and the percentages of Cu and Fe in the cut, the percentages of each mineral can be calculated.

	Bornite	Chalco-pyrite	Covel-lite	Chalco-cite	Pyrite	Total
#Rel.% Cu	30.6 (48.2 x 66.3)	15.5	1.0	0.6	--	47.7
% Cu in Cut No. 6 = 23.9						
% Cu of Total	15.3 $\left(\frac{30.6}{47.7} \times 23.9\right)$	7.8	0.5	0.3	--	23.9
% Mineral	23.9 $\frac{(15.3)}{66.3}$	22.5	0.7	0.4	--	--
#Amt. Fe %	2.7	6.9	--	--	6.1 (15.7 - 9.6)	15.7
% Fe in Cut No. 6 = 15.7						
% pyrite					13.6 $\frac{(6.1)}{46.6}$	

Amounts of Cu and Fe are calculated from the following:

	Bornite	Chalco-pyrite	Covel-lite	Chalco-cite	Pyrite
Cu %	66.3	34.5	66.4	79.8	--
Fe %	11.1	30.5	--	--	46.6
S %	25.6	35.0	33.6	20.2	53.4

From the abundance of the minerals and the weight of each cut, the actual % of each mineral in the cut is calculated.

For example: cut No. 6 Weight = 13.8 grams of 150 grams
= 9.4%

Percent of each mineral:

Cut No.	Bornite	Chalco-pyrite	Covel-lite	Chalco-cite	Pyrite
6	2.3 (9.4 x 23.4)	2.1	0.07	0.03	1.35

By the addition of the percent minerals of each cut, the percent minerals of the total is determined.

Cut No.	Bornite	Chalco-pyrite	Covel-lite	Chalco-cite	Pyrite
1	--	--	--	--	--
2	--	--	--	--	--
3	--	--	--	--	--
4	--	--	--	--	--
5	--	--	--	--	--
6	2.3	2.1	0.07	0.03	1.35
7	--	--	--	--	--
8	--	--	--	--	--
Total	26.1	26.9	0.8	0.6	12.4

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